Plant Oil Derived Monomers for Use in Materials

By

Deborah Woodcock

A thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry

University of Warwick, Department of Chemistry

October 2012

Contents

Acknowledgements

I would firstly like to thank my academic supervisor Dr Andrew Clark for his help and guidance throughout my time at Warwick, his help and knowledge have been invaluable. I must also thank my industrial supervisors, Dr Neal Williams and Dr Chris Lampard at Akzo Nobel for their expert knowledge on many aspects of my project. I would like to thank Dr Hugues Straub for his laboratory help in industry, as well as the analytical team at Akzo Nobel for much of the analysis run on samples in chapter 3. I would also like to extend my thanks to the many members of the Clark group past and present. In particular I would like to thank Seng Soi Hoong for his invaluable knowledge of oil chemistry and Dr Stuart Coles for his help right from my first experiment on day one.

Thanks must go to many members of the chemistry department, including Dr Adam Clarke, Dr Ivan Prokes and Edward Tunnah for the NMR service. To the mass spec service run by Dr Lijiang Song and Philip Aston and for the many high resolution mass spectra performed. I would also like to thank Dave Hammond for his help for the many TGA and DSCs he performed, Lara-Jane Pegg for AFM imaging and the Bon group and Science city for use of equipment.

Away from the university I would like to thank my friends and housemates that have put up with me for the last few years! Last but by no means least I want to thank my family especially my mum, dad and sister for their encouragement and support, with special thanks to Amanda for her ‘artistic’ input!

Declaration

The work presented in this thesis is the original work of the author. Reference to previous related results and ideas have been fully acknowledged. All work was performed in the Department of Chemistry at the University of Warwick and at Akzo Nobel between October 2008 and June 2012 and has not been submitted for a degree at any other institution.

Deborah Woodcock

Abstract

The majority of work presented covers an investigation in to vegetable oil based monomers for use in low 'volatile organic compounds' (VOC) or VOC free paints. Chapter 1 provides an introduction to recent EU legislation into the reduction of VOCs in a wide variety of paints and coatings. This is followed by an overview of vegetable oil based chemistry and subsequently the use of vegetable oils within materials, specifically coatings.

Chapter 2 discusses the synthesis of a selection of vegetable oil derived monomers using a number of different diamines and aminoalcohols to produce fatty amides with methacrylate, styrene and maleate functionalisation. A selection of 3 vegetable oils with varying degrees of unsaturation (soybean oil, rapeseed oil and cocoa butter) were trialled to see the effect the starting oil had on the subsequent monomers. Removal of some or all of the unsaturation within the fatty chains of the triglycerides and monomers was carried out, primarily as a way to potentially reduce yellowing often found in paints derived from a vegetable oil source.

Chapter 3 introduces the technique of emulsion polymerisation, followed by the incorporation of a selection of the methacrylate monomers synthesised in the previous chapter into polymer latexes. Comparisons of the latex properties are made and the results of a variety of tests (DSC, MFFT, hardness, yellowing ability) described. Comparisons between unsaturated and epoxidised derivatives are made and conclusions drawn.

Chapter 4 focuses on the preparation of polyurethanes (PU) from a small library of renewable diols. These were synthesised using both cocoa butter and rapeseed oil with diethanolamine, followed by epoxidation of the residual unsaturation in some

cases. These were reacted with MDI and a variety of commercial diols (PEGs and 1,4-butanediol) and their physical properties (tensile strength, Young's modulus, swelling and cross-linking density) and thermal properties analysed by a variety of methods (TGA, DSC).

Chapter 5 describes the $BF_3.Et_2O$ catalysed ring-opening of a small range of epoxidised oils derived from rapeseed and cocoa butter to give higher molecular weight pre-polymers/oligomers suitable as polyols for PU synthesis. Two approaches to the monomers are described.

Chapter 6 describes the experimental conditions and chemical analysis of the all the key reactions and processes described in the thesis.

Abbreviations

AFM – Atomic Force Microscopy

BMA – Butyl Methacrylate

Br - Broad

*t*Bu - *tert*-Butyl

d - Doublet

dd - Doublet of doublets

ddd - Doublet of doublet of doublets

ddt - Doublet of doublet of triplets

dt - Doublet of triplets

DCM -Dichloromethane

DSC - Differential Scanning Calorimetry

eq - Equivalents

ESI - Electrospray Ionisation

GPa – Giga Pascal

GPC – Gel Permeation Chromatography

HEMA - hydroxyethyl(meth)acrylate

HRMS - High Resolution Mass Spectroscopy

Hz - Hertz

IR - Infra-red

KDa - Kilo Daltons

m- Multiplet

MDI – Methylene diphenyl diisocyanate

MFFT – Minimum film formation temperature

mp - Melting Point

MS – Mass Spectrometry

nm – Nanometers

NMP - N-methyl pyrollidine

NMR - Nuclear magnetic resonance

Ph - Phenyl

ppm - Parts per million

q - Quartet

rt - Room temperature

s – Singlet

SDS – Sodium Dodecyl Sulfate

SM - Starting Material

t – Triplet

TDI – Toluene diisocyanate

Temp – Temperature

Tg – Glass transition temperature

TGA - Thermogravimetric Analysis

TLC - Thin Layer Chromatography

TMS – Trimethylsilane

VOC – Volatile Organic Compound

VOMM – Vegetable Oil Macromonomer

Chapter 1.0: Introduction

1.1 Need For Lower VOCs in Coatings

With recent EU legislations coming into force the amount of volatile organic compounds (VOC) used in paints and other decorative coatings has to be reduced significantly.[1] Directive 2004/42/CE of the European parliament and council is meant to limit the amount of VOCs in coatings that contribute to the formation of tropospheric ozone. Due to the nature and properties of the various coatings and varnishes available the reduction of VOCs is dependent on the coating. Examples include interior matt wall and ceiling coatings. These should have a maximum of 30 g/l, whereas trim varnishes and wood stains have a higher limit of 130 g/l in ready to use coatings. Organic solvents have traditionally been used in paints to aid with their fluidity and to help to give them their shiny smooth finish.[2] With these legislations in place paint manufacturers are looking to change the formulations of their paints to either move more towards waterborne systems[3] or to increase the solid contents in the existing formulations and thus have a lower percentage of organic solvent.

One focus of this project will be to incorporate novel vegetable oil based macro-monomers in to waterborne polymer dispersions via emulsion or miniemulsion polymerisation. The main focus on waterborne polymers for use in surface coatings was originally directed at the emulsion polymerisation of synthetic crude oil based monomers.[4] This was mainly due to the low cost, compatibility with the emulsion polymerisation process as well as low VOCs. This method is extremely useful now due to the new government legislation on the reduction of VOCs.

Paints and coatings are usually liquids and are used primarily to decorate or protect a surface. Although there are a number of different types of paint, there are two main

types of decorative paints, solvent based and water-borne based. They are commonly made up of a number of different components; traditionally these are the diluent or solvent, pigment and the binder or vehicle. The solvent is used to control the viscosity of the paint along with helping with the application. It is not a compulsory part of the final coat and eventually evaporates to leave a solid film behind.

One of the most important components is the binder. This is what allows for adhesion of the paint and also strongly influences a lot of the properties and final finish of the coating. It is the binder that contains the resin which can either be synthetic or natural; examples can include polyurethanes, acrylics, alkyds and epoxies.

The drying or curing of paints can occur in a number of different ways depending on their type. Polyurethanes cure *via* polymerisation to form a cross-linked polymer coat, epoxies also fall into this category and alkyds cure *via* oxidative cross-linking. This is also the method used by drying oils (see page 19). Waterborne coatings dry in a different way, utilising the evaporation of water, bringing the polymer 'particles' closer together, allowing for deformation followed by coalesence.[5]

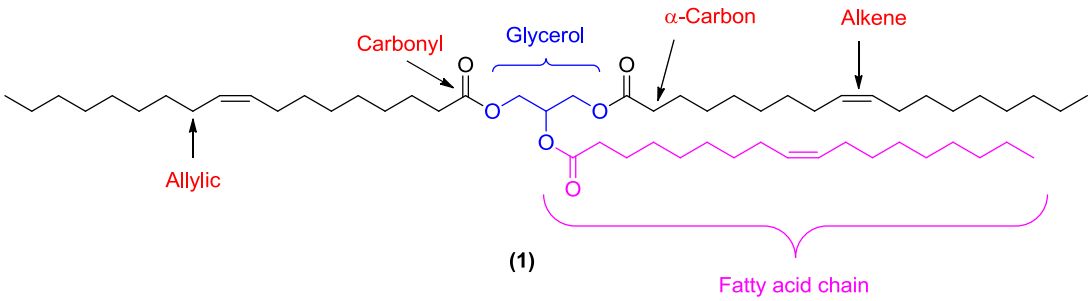
Before the wide availability of mineral oil and its fractions, fats and oils of vegetable and animal origin were used widely for many non-food applications such as in lamps and as lubricants. Basic oleochemicals can be produced from these oils and fats which also have many uses, including candles, cleaning agents, make-up, pharmaceuticals, plastics and paints,[6] with the earliest type of house paints being made mainly of linseed or tung oil with zinc or lead oxide.[7] Due to the discovery and availability of mineral oils there has been a steady decrease in the amount of renewable raw materials used, and by the mid 1990's the use of oils and fats in these

applications was less than a third of what it had been in the 1950's.[8] In general ~90 % of all chemicals today are derived from fossil fuels, with the chemical industry being the third highest user of this feedstock, behind energy and transportation uses.[9-11]

More recent research has investigated the use of vegetable oils as 'greener' alternatives to crude oil based monomers.[12,13] Vegetable oil based monomers have not traditionally been used for water based coatings due to their hydrophobicity, so research is currently looking into the incorporation of these hydrophobic monomers into these systems.

1.2 Vegetable Oils

Vegetable oils **(1)** are part of a family of compounds known as lipids. Lipids are comprised of many compounds including fats, sterols, complex glycerolipids and most importantly for this project triglycerides, of which vegetable oils are one. Triglycerides as the name suggests are comprised of a glycerol component and three fatty acid chains (Figure 1.1) and make up a large majority of vegetable oils; monoglycerides, diglycerides and free fatty acids are also found.



(1)

Figure 1.1: Triglyceride showing areas of functionality suitable for further chemical transformation

There are many naturally occurring fatty acids, many of which can be found in vegetable oils and animal fats. There are both saturated and unsaturated fatty acids (Figure 1.2), the former of which are more abundant in fats and the latter in vegetable oils.[14] Fatty acids can be identified with a number (e.g. C18:1 for oleic acid), with the first number corresponding to the length of the carbon chain, and the second number corresponding to the number of double bonds found within the chain.

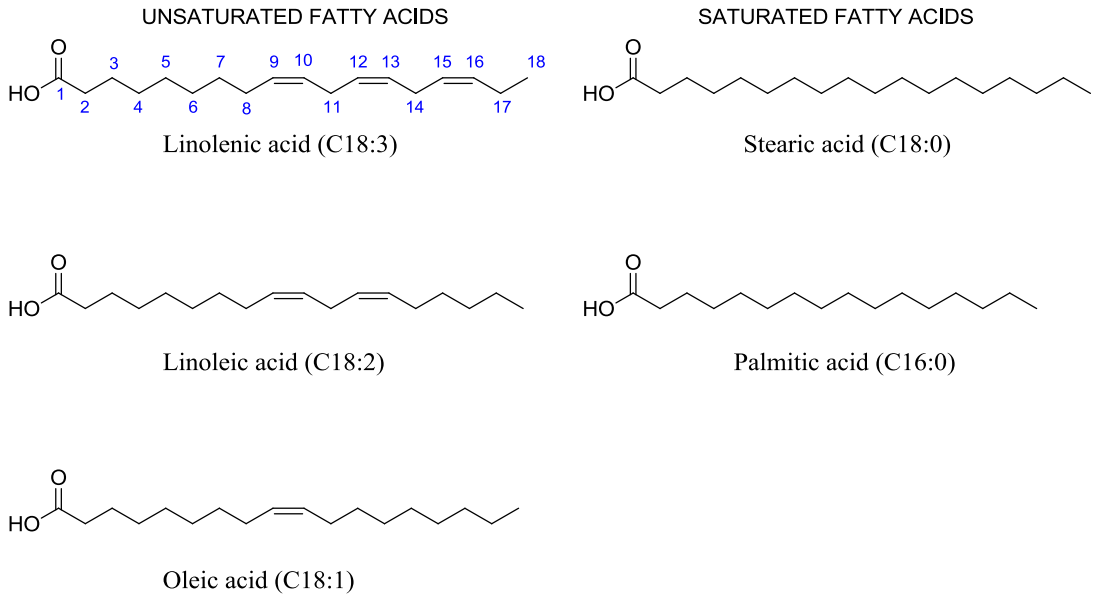


Figure 1.2: Most abundant saturated and unsaturated fatty acids

Triglyceride	% of 16:0	% of 18:0	% of 18:1	% of 18:2	% of 18:3
Cocoa Butter	26	34	35	-	-
Corn	13	3	31	52	1
Cottonseed	23	2	17	56	-
Linseed	6	3	17	14	60
Olive	10	2	78	7	2
Palm	44	4	39	11	-
Rapeseed	4	2	62	22	10
Safflower	7	3	14	75	-
Sesame	9	6	41	43	-
Soybean	11	4	23	53	-
Sunflower	6	5	65	26	-

Table 1.1: Typical fatty acid compositions over a selection of triglycerides[6]

1.3 Chemistry of Triglycerides

Triglycerides have many centres amenable to chemical reactions; these include the ester carbonyl component, the α-carbons, the allylic carbons and the alkenes found in the unsaturated chains, (see Figure 1.1). One current main use of triglycerides is their transformation into methyl esters for use as a fuel source, known as biodiesel. Different countries use different oils for the production of their biodiesel, (see section 1.3.2.1).

Particularly relevant to this project, is the chemistry of the alkene and allylic groups found in triglycerides. *The presence of traces of unsaturation in paint coatings is thought to be one of the factors involved in the yellowing of paint over time and this will be investigated further in Chapter 3.*[15] As a consequence, a brief summary of the chemistry of triglycerides is presented. This is not designed to be exhaustive but should give the reader an overview of the subject.

1.3.1 Reactions at the Alkene Functionality

1.3.1.1 Hydrogenation

It is possible to completely remove the unsaturation in triglycerides and fatty acid derivatives *via* hydrogenation. The hydrogenation of edible oil was first reported in 1902.[16,17] This is a well-known process and it is used substantially in both the chemical and the food industries.[18] Within oil chemistry this process is also referred to as 'hardening'[14] and has been the focus for much research.[19,20] Typically this process is carried out by using molecular hydrogen and a catalyst, such as nickel[21] or palladium.[16,22,23] A typical method to prepare margarine involves soybean oil being

exposed to 120 °C under 300 bar of hydrogen gas with a nickel based catalyst made from powdered nickel pressed with one or more group VI element.[24]

Selective reduction of only one alkene in a polyunsaturated molecule (e.g. linoleic acid **(2)**) has been reported using palladium nano-particles prepared by reduction of $PdCl_2$ in an aqueous buffer. Due to the health issues with *trans* fats, the desired result in nutritional terms would be to have a *cis* double bond (*Z*)-**(3)**,[25] however in most cases you get mixtures with the *trans* product (*E*)-**(3)**, (Figure 1.3). The size of ruthenium[26] and platinum nanoparticles[27] has been shown to parallel the reactivity in the hydrogenation of soybean and palm oil respectively. The smaller particle sizes correlated with more selective reductions.

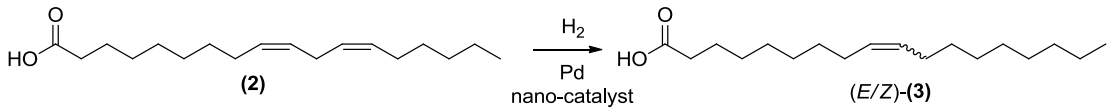


Figure 1.3: Selective hydrogenation of linoleic acid

Hydrogenation can be used to produce biodiesels with higher oxidative stability without compromising thermal stability[28] and cold flow properties.[29,30] Souva *et. al.* investigated the use of a high activity catalyst Pd/ImS3-12@Al_2O_3 which showed higher hydrogenation activity than the conventional Pd/C catalysts, but also the ability to selectively reduce polyunsaturated derivatives to the monoene products.[29] In biodiesel manufacture *cis*-products are preferred due to possessing lower crystallisation points than their *trans* alkenes derivatives.[29] Very recently, copper oxide catalysts have been used as bifunctional catalysts for both transesterification (see section 1.3.2.1) and selective hydrogenation of highly polyunsaturated hempseed triglycerides to give biodiesel.[31]

1.3.1.2 Epoxidation

Perhaps the next most important reaction with regards to oil chemistry is the epoxidation of the unsaturation within the fatty acid chains (e.g. **(4)**). This is useful as it gives potential for further functionalisation of the triglycerides for many different purposes.

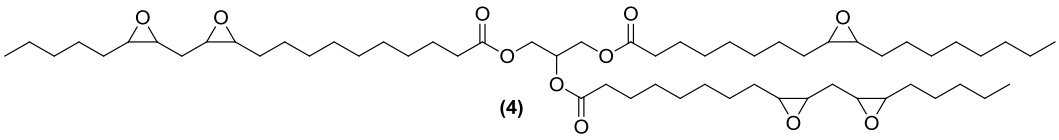


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Figure 1.4: Epoxidised Soybean oil (4)

There are many methods of epoxidation, one of the most common is the use of peroxide-containing reagents such as *meta*-Chloroperoxybenzoic acid (mCPBA), known as the Prilezhaev reaction.[32] Industrially, epoxidation is carried out by the Cargill process where peracetic acid (prepared from acetic acid and H_2O_2) is used (see section 1.3.1.4).[33,34] There are also many catalytic methods of epoxidation which utilise H_2O_2 as an oxidant with transition metal compounds as catalysts. Du *et al* [35] studied the epoxidation of methyl linoleate with catalytic amounts of methyltrioxorhenium (4 mol%) along with pyridine and H_2O_2 over 4 h. The catalyst loading could be lowered to as little as 1 mol% at the expense of the time taken to reach full conversion. A recent paper by Petrović *et al* reported the epoxidation of soybean oil utilising peroxoacetic acid or peroxoformic acid in the presence of amberlite, an ion exchange resin, in toluene.[36] Campanella *et al* completed a study into the use of amorphous Ti/SiO_2 as a catalyst used in conjunction with H_2O_2 in the presence of *tert*-butanol for the epoxidation of soybean oil and its methyl esters. The highest yields were afforded with a molar ratio of 1.1:1.0 H_2O_2:substrate.[37]

Other methods of epoxidation include the use of tungsten-based catalysts[38](see section 2.5) and the use of enzymes.[39] Epoxy alkylstearates have been prepared by a lipase catalysed esterification and peracid formation from oleic acid followed by epoxidation of oleic acid in a one-pot reaction.[39] The epoxidation step is shown in Figure 1.5. The reaction mixture also contains an alcohol which allows the epoxystearic acid to undergo lipase catalysed esterification to give epoxystearic acid alkyl ester.

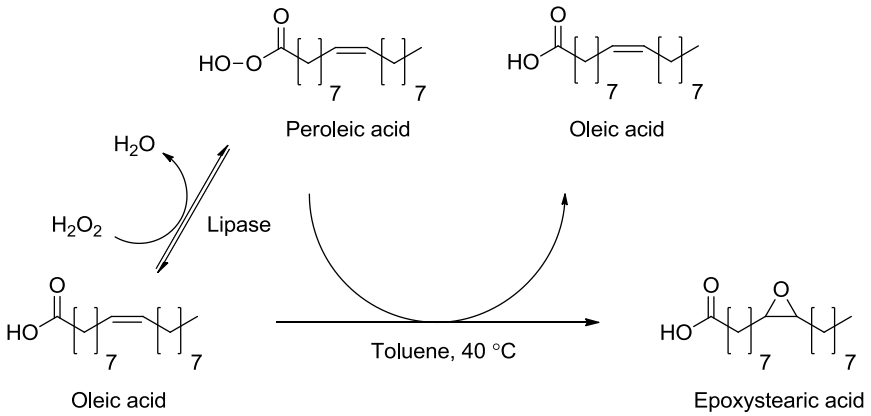
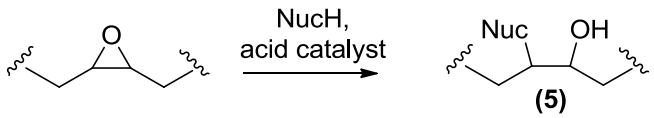


Figure 1.5: Synthesis of epoxy alkylstearates

1.3.1.3. Nucleophilic Ring-Opening of Epoxides

Epoxides are a relatively strained species and as such are more reactive than other ethers; due to this they can easily undergo nucleophilic ring-opening. Usually the products gained from ring-opening are alcohol derivatives **(5a-g)**. A number of different nucleophiles can be used in the ring-opening procedure, normally with an acid catalyst, these include water **(5a)**,[40] alcohols **(5b)**,[41] amines **(5c)**[42] and thiols **(5d)**.[43]



Nuc = **(a)** OH, **(b)** OR, **(c)** NR_2, **(d)** SR, **(e)** Br, **(f)** Cl, **(g)** NEt_2

Figure 1.6: Nucleophilic ring opening of epoxides

Guo *et al* studied the ring-opening of epoxidised soybean oil in a mixture of methanol, water, isopropyl alcohol and fluoroboric acid. The mixture was stirred at 50 °C for an hour, followed by the addition of ammonia to quench the reaction.[44]

Diethylamine has been reported as a nucleophile in a method to ring-open epoxidised soybean oil catalysed with the Lewis acid $ZnCl_2$. Reacting the ESBO for 4 h at 90 °C gave an 80 % yield of amine functionalised polyol **(5g)**. Halogen nucleophiles have been used to prepare β-hydroxy halo triglycerides **(5e-f)**[45] which were used as monomers to make polyurethanes.[44]

1.3.1.4 Dihydroxylation

Direct dihydroxylation of alkenes is another extremely useful transformation of fatty acids and triglycerides, (Figure 1.7). The use of high oxidation state osmium and ruthenium based catalysts are common in the direct dihydroxylations of organic olefins, including the asymmetric Sharpless dihydroxylation.[46-49]

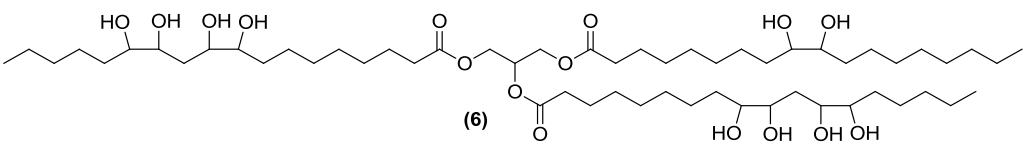


Figure 1.7: Dihydroxylated soybean oil

However, there is substantial literature where dihydroxylation occurs *via* ring-opening of an epoxidised product as an intermediate. This is a special case of the reaction described in section 1.3.1.3, where epoxidation and ring-opening occur in the same pot. One such example is demonstrated by Oakley *et al* where unsaturated fatty acids were first epoxidised using H_2WO_4 as a catalyst with *tert*-butanol, H_2O_2 and O_2, followed by ring-opening to give diols. If further equivalents of O_2 or H_2O_2 were added oxidative cleavage of the intermediate diol **(7)** occurred to give two carboxylic acid derivatives **(8)** and **(9)**, (Figure 1.8).[50]

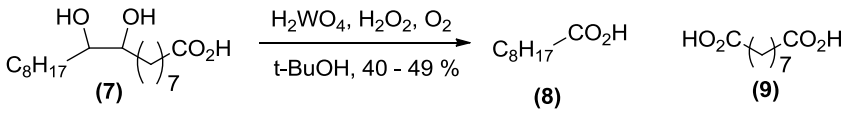


Figure 1.8: Further C-C bond cleavage after dihydroxylation of fatty acid.

Another important method for production of diols or polyols is the Cargill patented method.[33] This method involves the epoxidation of partially hydrogenated soybean oil using peroxyacetic acid to give **(4)**. The partially hydrogenated, fully epoxidised oil is followed by a ring-opening step utilising methanol and HBF_4 as a catalyst to give **(6)**. These polyols are then taken on to form polyurethanes using TDI.

Reaction of unsaturated triglycerides in an emulsion with W powder, H_2O_2 and H_3PO_4 in water at 100 ˚C in the presence of adogen (a phase transfer catalyst) for 4 hours furnished diols **(6)** *via* the intermediacy of epoxidised oils **(4)**. If the reaction was carried out at room temperature or at 40 ˚C only epoxide **(4)** was isolated.[51,52]

1.3.1.5 Metathesis

Catalytic metathesis processes were originally noted in a paper by Banks and Bailey in 1964,[53] when reporting that propylene could be 'disproportionated' to ethylene and also *n*-butanes. Since then it has become a very useful tool in organic chemistry and materials chemistry.[54] The first reported metathesis of oleochemicals was the self-metathesis of methyl oleate **(10)** using the WCl_6/Me_4Sn catalyst system.[55] Since then it has been used in the metathesis of linoleate and linolenate,[56] Since this initial report, other catalytic systems have been described for fatty acid self-metathesis reactions based around Re_2O_7/Al_2O_3[57] and $Re_2O_7/SiO_2.Al_2O_3/SnBu_4$[58] and finally with the development of such catalysts as Schrock and Grubbs.[59,60]

Ngo and Foglia in 2006 investigated the self-metathesis of oleic acid **(10)** to give alkene **(11)** and diacid **(12)** in a solvent free process using a second generation Grubbs catalyst (Figure 1.9).[61] This study improved upon previous reports using ruthenium catalysts in solvent based processes where conversions were low.[55] This method was also found to work on fatty acids incorporating other functional groups such as ricinoleic acid containing a C-12 hydroxyl group.

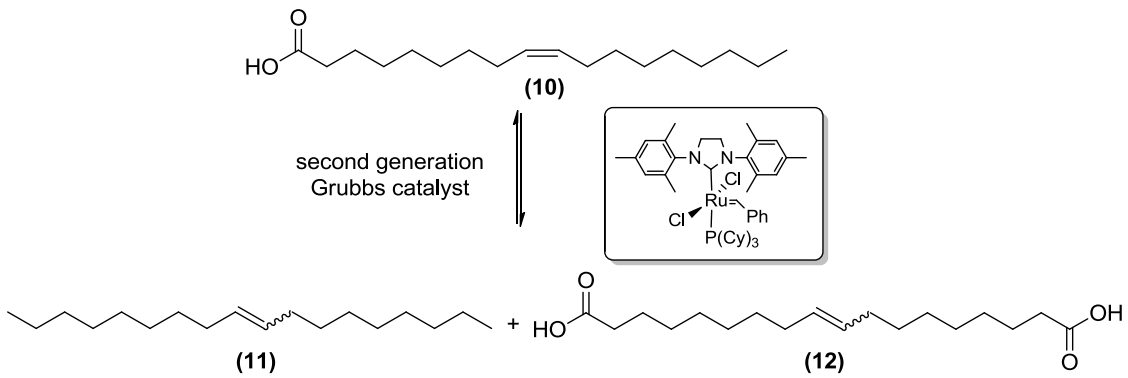


Figure 1.9: Self-metathesis of oleic acid[61]

The WCl_6/Me_4Sn process was also the first catalyst system to be used with an oleochemical in a cross-metathesis reaction. The reaction between methyl oleate and hexene produced dodec-9-enoic acid methyl ester and dodec-3-ene in only 20% yield.[62] One useful and highly investigated cross-metathesis reaction is the reaction of oleochemicals with ethene, for example with triolein **(13)** (Figure 1.10). The novel triglyceride **(14)** produced can undergo formal addition of water to give triol **(15)** which has been used in PU synthesis.[54] This 'ethenolysis' reaction has also been used successfully in yielding monomers for polyesters, polyamides and polyethers.

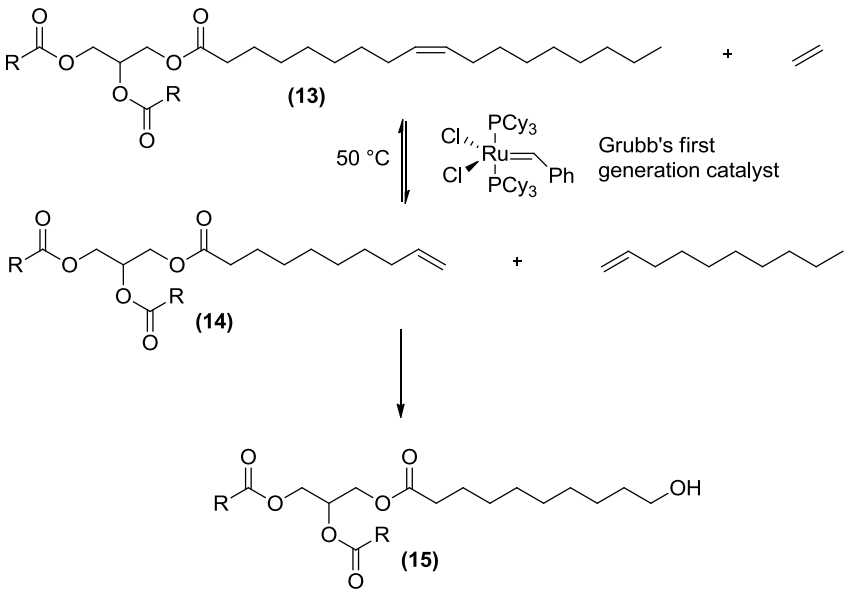


Figure 1.10: Cross-metathesis of triolein with ethene

Other developments in the field include the cross-metathesis of fatty acid derivatives, such as methyl oleate with more functionalised species such as acrylates, acrylonitiles and allylic compounds.[63-65] Work reported by Jackson and Robinson, spans both cross and self metathesis, with examples including the cross-metathesis of natural oils with 2-butene.[66]

1.3.1.6 Ozonolysis

Ozonolysis is a relatively clean way to cleave the fatty acid chains oxidatively at the unsaturation points. Petrovic has studied the reductive ozonolysis of soyabean oil at -40 ˚C in CH_2Cl_2 and MeOH as solvent using $NaBH_4$ as a reductant. The polyols produced have similar structures to **(15)** and have been used to manufacture polyurethanes[67] and polyesters.[68] Work by Tran *et al*[69] also looked into the synthesis of polyols from soybean oil using an ozone mediated method with various catalysts including NaOH, pyridine, 4-DMAP and $CaCO_3$ at 0 °C.

An example of the only current industrial use of this reaction within oil chemistry is the transformation of oleic acid **(10)** into azelaic acid **(16)** and pelargonic acid **(17)**. The former can undergo further hydrogenation to produce nonane-1,9-diol **(18)**[70] (Figure 1.11), an interesting monomer for polyester or polyurethane synthesis.[71]

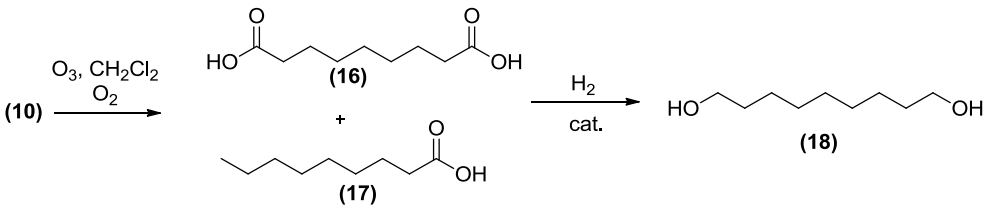


Figure 1.11: Ozonolysis of oleic acid to azelaic acid and subsequent hydrogenation to nonane-1,9-diol (Commercial catalysts are used e.g aluminium-zinc or copper-chromium etc).

1.3.1.7 Other Oxidations

Unlike ozonolysis, oxidation of the alkenes of fatty acids and triglycerides can also be accomplished without cleavage of the carbon chains. In particular the introduction of a ketone or aldehyde at this position is possible.[72] The Hoechst-Wacker process was originally applied to the oxidation of ethylene giving

acetaldehyde using tetrachloropalladate as a catalyst utilising oxygen and water.[73] Hermans *et al* has since reported a one-step metal free route to the ketonised unsaturated fatty methyl esters **(20)** and **(21)** and triglycerides which was afforded with nitrous oxide.[74]

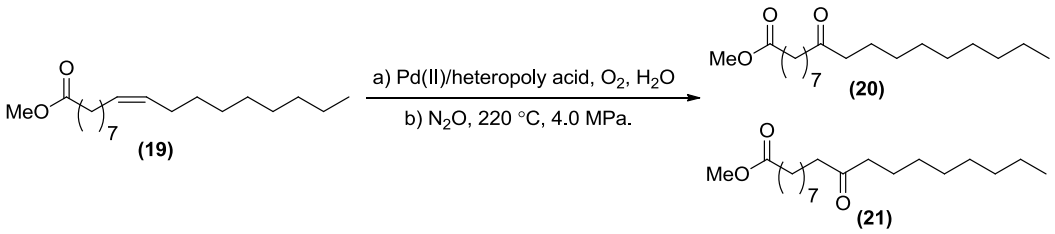


Figure 1.12: Methyl oleate (19) undergoing the Wacker reaction using traditional 'Wacker' conditions and (b) the metal free conditions by Herman *et al*

Other notable reactions with the double bond in fatty acids and triglycerides include hydroformylation,[75] also known as the oxo process, which adds an aldehyde onto the chain **(22)** hydrosilylation which adds an Si-H across the double bond **(23)**,[76] and hydrovinylation **(24)**, (Figure 1.13). Hydroformylation has been achieved industrially in the Dow Chemical process to make polyols from vegetable oils.[77] In this way hydroformylation of methyl oleate **(19)** is achieved with a 1:1 mixture of H_2 and CO gases under rhodium based catalysts to give methyl 9-formyloctadecanoate **(22)**.

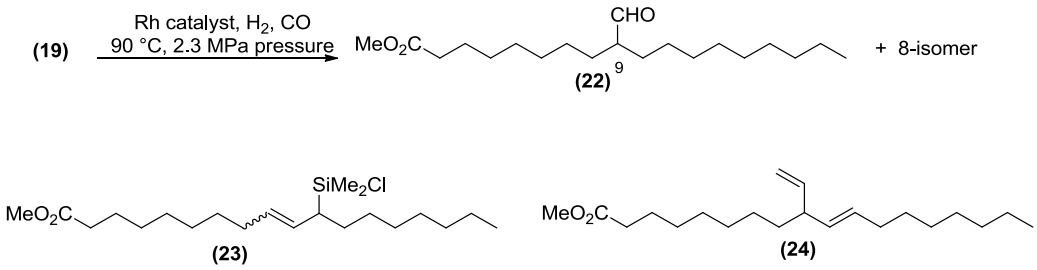


Figure 1.13: Hydroformylation of methyl oleate (19) and other hydrosilylation (23), and hydrovinylation (24) products from pre-conjugated methyl linoleate[14]

1.3.1.8 The Thiol-ene Reaction.

The thiol-ene reaction is often regarded an example of 'click chemistry' which was first reported by Sharpless *et al.*[78,79] The thiol-ene reaction has been successfully applied in the production of polyols from fatty acids and triglyceride derivatives. Hence, methyl oleate **(19)** can be reacted with 2-mercaptoethanol with 2,2-dimethyoxy-2-phenylacetophenone (DMPA) as a photo initiator under UV irradiation to give a mixture of hydroxylated products **(25**), (Figure 1.14). Reduction of **(25)** with $LiAlH_4$ yields polyols which have been used in polyurethane chemistry.[80] This approach has been extended to triglycerides, such as triolein.[81] Thiol based chemistry has also been used to successfully produce soybean oil based UV curable coatings.[82] These were afforded by the ring-opening of epoxidised soybean oil to give **(26)** with multifunctional thiols (Figure 1.14), which could then undergo UV curing with acrylates.

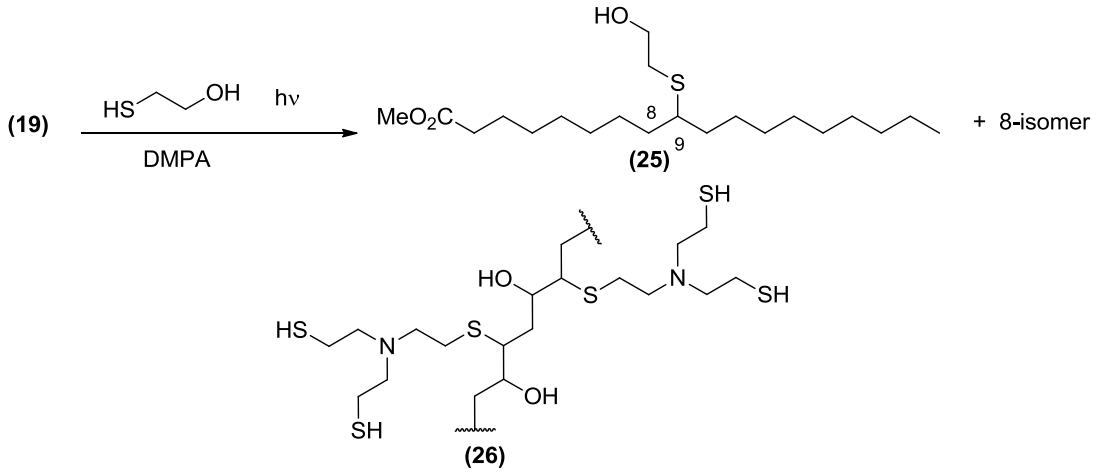


Figure 1.14: Addition of thiol *via* epoxides ring opening of methyl oleate (19) and soybean based thiol (26) for UV curing.

1.3.2 Reactions at the Carbonyl

1.3.2.1 Transesterification

Reactions at the carbonyl position of fatty acids and triglycerides are the 'classical' approach to oleochemistry. One such reaction is glycerolysis which involves the reaction of triglycerides with glycerol in varying ratios to give both mono- and di-glycerides, (Figure 1.15).[83]

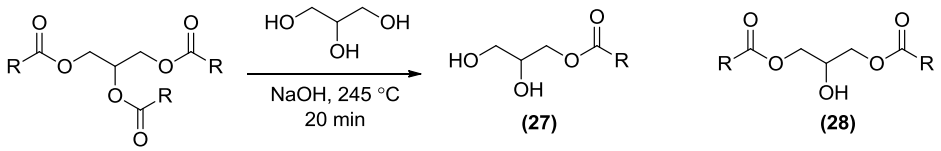


Figure 1.15: Glycerolysis of triglcerides

An extremely useful reaction is the transesterification of vegetable oils with methanol to produce a methyl ester, and glycerol.[84] This involves reacting a triglyceride with methanol and a catalyst such as sodium methoxide or potassium

hydroxide. The reaction is not just limited to methanol; many other alcohols can also be used to synthesise a range of different esters. This is an extremely crucial reaction in the production of biodiesel, (Figure 1.16).[85]. Although a large range of alcohols can be used in the process, ethanol and methanol are most commonly used due to their low costs. Significant research has been reported into optimising the transesterification process by tailoring catalyst and temperature.[86] While alkali catalysed transesterification generally provides faster and higher yielding reactions, acidic catalysed and enzyme catalysed methods are also possible.[87,88] The use of branched alcohols, such as isopropanol and 2-butanol, has been shown to reduce the crystallisation temperature of the fuel.[89]

Figure 1.16: Synthesis of biodiesel

As well as transesterification being used for the production of biodiesel there have been a number of other methodologies[90] including microemulsion,[91] and pyrolysis techniques.[92] Another method for renewable fuels that involves no chemical processing is dilution.[93] This involves vegetable oil being blended with diesel fuel; however transesterification still remains the favourite in part due to lower viscosities of the ester products and low costs.[94]

1.3.2.2 Aminolysis

A similar reaction can take place between triglycerides and amines giving fatty amide products, (Figure 1.17). Gast *et al* reacted linseed oil and diethanolamine **(29)** at 110-115 °C with sodium methoxide as a catalyst.[95] These *N*,*N*-bis (2-hydroxyethyl) linseed amides **(30)** were then taken on to produce a number of viscous oil polyesters, for use in protective coatings by heating with different dibasic acids, ranging from terephthalic to brassylic acid in xylene. All polyesters were tested for their film properties after both baking at 190 °C and after air drying.[95]

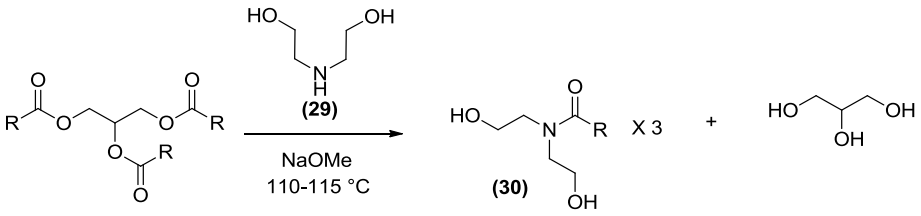


Figure 1.17: Example of amidation with (29) to give fatty amides

1.3.3 Reactions with the Fatty Carbon Chain at the Allylic Carbon and C-2.

The current thesis will involve utilising the chemistry of triglycerides by reaction at both the alkene functionality (section 1.3.1) and the ester functionality (section 1.3.2) and as a consequence we have discussed this chemistry in detail in sections. However, there are other points of reactive interest within vegetable oils and fatty acids, which are mentioned briefly below. The first is functionalisation at the allylic carbon this is a potential active site for oxidation, and is important for the process of autoxidation (discussed in **1.4.1.1**) but it can also undergo reactions which can include allylic hydroxylation[96] and halogenation.[97] Hence, oleic acid has been reacted with SeO_2 and *t*-BuOOH to give a mixture of 8- **(31)** and 11-hydroxy-9(*E*)-

octadecanoic **(32)** acids and the 8,11-dihydroxy analogue **(33)** as a mixture of diastereomers,[98] (Figure 1.18).

Functionalisation at the α-carbon (C-2) is readily achieved either anionically (*via* formation and reaction of the corresponding enolates or enols) or radically *via* the intermediate of an enolate radical.[6]

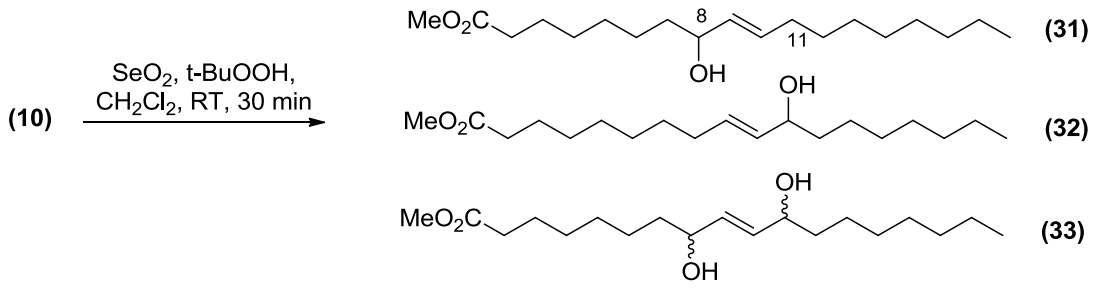


Figure 1.18: Allylic oxidation of methyl oleate (10)

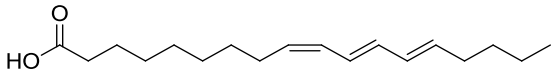
1.4. Vegetable Oils in Materials

Vegetable oils have been used extensively in various materials, especially coatings, for a number of years.[99,100] Historically vegetable oils were used in paints and other coatings long before mineral oil became widely and cheaply available. This field is vast and we will concentrate on advances in coatings. The use of vegetable oil derivatives in polyurethanes will be discussed later, in chapter 4.

1.4.1. Non-Chemically Modified Vegetable Oils

1.4.1.1. Drying Oils

Triglycerides themselves are able to polymerise without the need to functionalise them further (e.g. by epoxidation, or addition of acrylates). A drying oil is one which with exposure to air will gradually become tough and form a solid film; examples of these oils include linseed oil, poppy seed oil and tung oil. These triglycerides are predominately made up of unsaturated fatty acid chains usually with 2 or more alkenes. For example a prominent example of a drying oil is linseed oil. Linseed oil is made up of ~50% linolenic acid which contains 3 alkenes. Another example of a drying oil, tung oil, contains another triply unsaturated fatty acid this time in the form of α-eleostearic acid **(34)** which contains both *cis* and *trans* alkenes, (Figure 1.19). Tung oil is ~80% α-eleostearic acid. These oils have been used within the paint and varnish industry for many years.[101]



(34)

Figure 1.19: α-Eleostearic acid containing one cis and two trans double bonds

A semidrying oil also hardens when exposed to air however not to the same extent as the drying oils; examples of these types of oils include corn, cottonseed and sesame oils. These triglycerides contain no, or considerably less, triene groups such as **(34)**, and are made up substantially of linoleic **(2)** and oleic **(10)** acids.

Autoxidation, (see Figure 1.20) is the process responsible for the curing in both of these types of oils. The reactivity of a drying oil is usually denoted by its iodine value. A drying oil typically has an iodine value of higher than 130, a semi-drying oil is usually between 100 and 130 and a non-drying oil less than 100.[102]

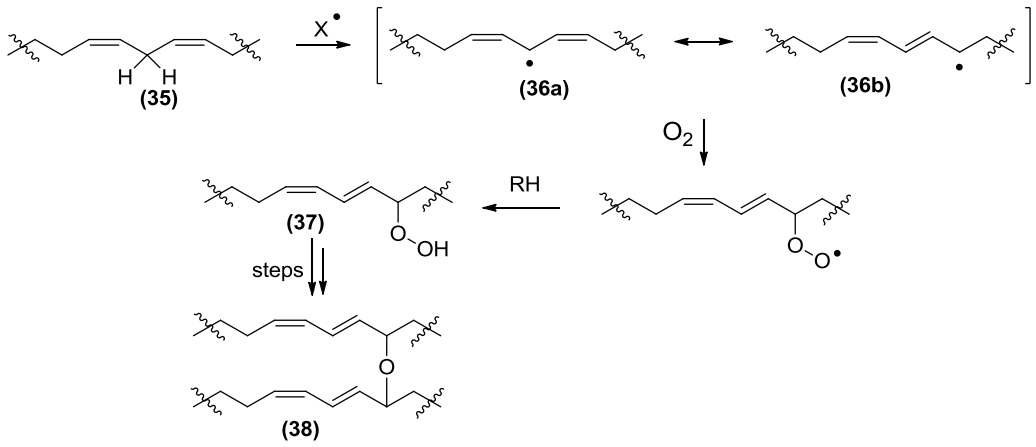


Figure 1.20: Process of Autoxidation in drying and semi-drying oils

Autoxidation of drying oils is a radical process that generally starts with the abstraction of hydrogen atom from the activated methylene group between two alkenes in a polyunsaturated chain **(35)** to give a resonance stabilised radical (**(36a)** ↔ **(36b)**). During this process conjugation of the double bonds occurs, and after reaction with O_2 leads to the production of hydroperoxides **(37)**. A number of steps can then lead to oligomerisation between fatty acid chains *via* ether linkages **(38)**. It is thought that this process is one of the main contributing factors to the yellowing colour that appears in paints over time. Full drying of these oils however can be quite slow, so 'driers' are often added. These are usually a metal salt derived from cobalt or iron.[103] By-products from oxidation include aldehydes. Recent research by Fjällström *et al* has looked into the effects of a range of external factors such as temperature on emissions of aldehydes during the drying of linseed oil paints.[104] This is topical, as with the increase in the inclusion of vegetable oils into coatings the health effects and toxicity of volatile aldehydes should be addressed. The emission of aldehydes was first noticed when linseed oil paints were reintroduced into the Swedish market in the late 1980's. It was found that paints rich in linoleic acid gave off hexanal while those rich in linolenic acid gave off propanal. Drying conditions at

elevated temperature and humidity levels appeared to speed up and increase the emissions of toxic aldehydes.

1.4.1.2 Use of Vinyl Monomers in Cross-Linking of Vegetable Oils

Drying and semi-drying oils can be copolymerised with a variety of activated vinyl monomers.[105] Styrene, divinylbenzene, α-methylstyrene or cyclopentadiene are vinylic monomers that are most commonly used in this approach, (Figure 1.21).[106] Typically free radicals are formed *via* thermal decomposition, either with or without an initiator depending on whether the oil is conjugated or not.

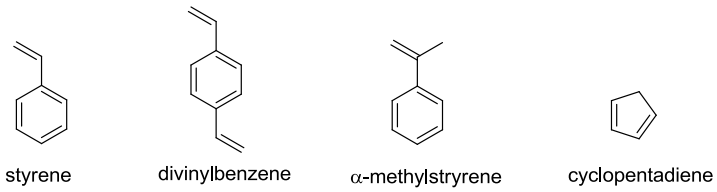


Figure 1.21: Styrene and divinylbenzene, α-methyl styrene and cyclopentadiene

Larock *et al* investigated the cross-linking of various oils *via* the copolymerisation of triglycerides with vinyl monomers using the initiator $BF_3.OEt_2$ in a cationic approach.[107-112] The majority of their studies were on fish oil, although linseed, tung and soybean were also investigated.[113-116] Comparisons were made between both conjugated and non-conjugated oils, with the non-conjugated oils tending to give stiffer thermoset polymers. Glass transition temperatures for the various polymers synthesised ranged from 11 °C to 113 °C depending on the combination of oil and styrene derivative used. The copolymerisation of oils with styrene was investigated both on their own and blended with other oils as before; a wide range of properties being recorded. Glass transition temperatures and moduli were recorded for an

investigation into corn oil based copolymers with glass transition temperatures ranging from 0 °C to 105 °C and tensile strength ranging from 6 to 2000 MPa, which are comparable to commercial petrochemical based polymers.

1.4.2 Chemically Modified Vegetable Oils

The effects of cross-linking in pre-modified vegetable oils has also been investigated. Gultekin *et al* have reported co-polymerisation of acrylate modified castor and linseed oils with styrene initiated by benzoyl peroxide,[117] whilst Akbas *et al* undertook similar research but with methyl methacrylate modified soybean and linseed oils with styrene again using benzoyl peroxide.[101]

Can *et al* [118,119] have investigated soybean and castor oil based monomers synthesised *via* alcoholysis with both aliphatic and aromatic alcohols including pentaerythritol and bisphenol A propoxylate. These were then further reacted with maleic anhydride to give **(39)** and **(40)** respectively, castor oil was also directly maleinized *via* reaction of its naturally occurring hydroxyl groups with maleic anhydride to give **(41),** (Figure 1.22).

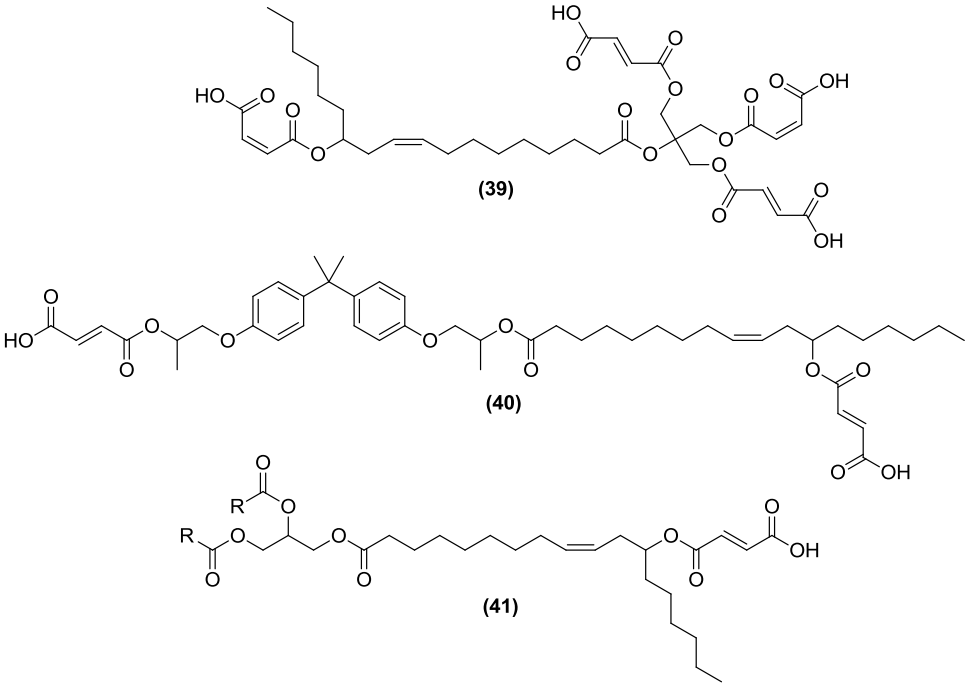


Figure 1.22: Castor oil pentaerythritol glyceride maleates (39), castor oil bisphenol A propoxylate maleates (40) and castor oil maleates (41).

These maleinized monomers **(39-41)** were then copolymerised with styrene[118] to produce hard rigid thermosetting polymers.[119] They gave a range of moduli from 0.8 to 2.5 GPa with Tg ranging from 72 to 152 °C. Results indicated that the castor oil gave better moduli, strength and Tg in comparison to soybean based derivatives.

The Wool group at the University of Delaware have also synthesised maleinated **(42)** and acrylated **(43)** monomers derived from triglycerides, (Figure 1.23).

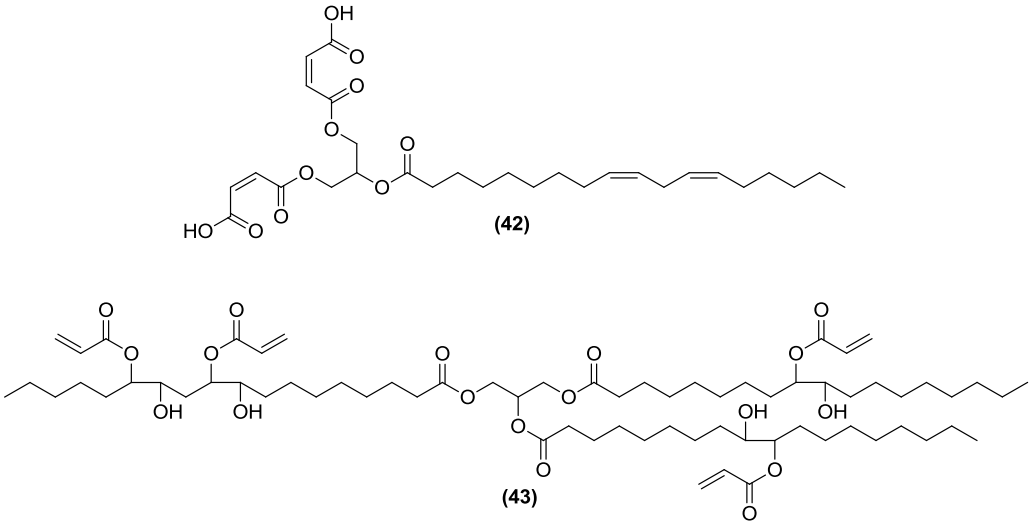


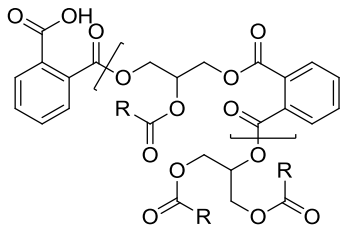
Figure 1.23: Maleinated soybean oil monoglyceride (42) and acrylated soybean oil (43).

The maleinated soybean oil monoglyceride **(42)** was synthesised in a two-step process. First monoglycerides were prepared *via* glycerolysis by reacting soybean oil with glycerol at 230 °C in the presence of calcium hydroxide as a catalyst under a nitrogen atmosphere. Maleinization of these monoglycerides was then carried out with maleic anhydride at 80 °C in the presence of triphenyl antimony and hydroquinone. The modified maleates **(42)** were then reacted with styrene to make copolymers.[99] The acrylated monomers **(43)** were prepared from epoxidised soybean oil *via* ring-opening with acrylic acid.

Günduz *et al* also investigated the maleinization of oils for use in resins and coatings. In this study, waterborne polyurethanes were synthesised using maleinized monoglyceride, hydroxyl-terminated polybutadiene, toluene diisocyanate and ethylene diamine.[120]

1.4.3 Alkyds

Alkyds are a family of coatings which have long since incorporated vegetable oil derivatives, usually in the form of fatty acids. These have been used since the late 1920's, and are one of the oldest polymer coatings incorporating vegetable oils.[12,105,121] Alkyd coatings **(44)** are comprised of polyhydroxy acids and polybasic alcohols and are a type of polyester. In a lot of cases these coatings can be modified with fatty acids, or mono-glycerides, which have been afforded from the alcoholysis of vegetable oils. The most abundant source of these acids is from triglycerides, hence these oils being a raw material for this type of coatings. Alkyds are predominately synthesised *via* the condensation polymerisation of acids and alcohols producing a highly branched polymer with a polyester backbone, (Figure 1.24).[122] The curing of these applied coatings then takes place *via* cross-linking of the alkyd chains, as seen with the autoxidation process of the drying oils, (see section, 1.4.1.1, Figure 1.20). Another method of curing includes utilising reactions of the residual hydroxyl groups within the polymer; however this is only efficient at high temperature drying conditions e.g. 80-200 °C. Variation of the oils and fatty acids used in these coatings allows for air drying times to be optimised, highly unsaturated chains would be preferable e.g. linolenic acid.



(44)

Figure 1.24: A generic Alkyd resin structure made up from a monoglyceride and phthalic anhydride.[122]

Alkyds can be classified based on the percentage of oil used in their formulation, they are defined as 'long', 'medium' or 'short'. Alkyds containing above 60% oil are classed as a long oil alkyds, between 40-60% are medium oils, and less than 40% oil is a short oil alkyd.[105] Some of the best drying times and water resistance can be obtained using soybean oil along with maleic anhydride.[105]

Not only has the effect of variation in the oils and fatty acids used in alkyd paints been investigated but Aydin *et al*[123] determined the effects of various anhydrides on alkyd film properties and viscosities, (Figure 1.25). Two different methods of alkyd preparation were used, the conventional method including alcoholysis of the oil and subsequent reaction with phthalic anhydride and a modified method where partial glycerides were synthesised from sunflower oil and glycerol and washed to remove excess glycerol before reacting with a range of anhydrides. Removing the excess glycerol in the modified method seemed to give alkyds with better film properties.[123]

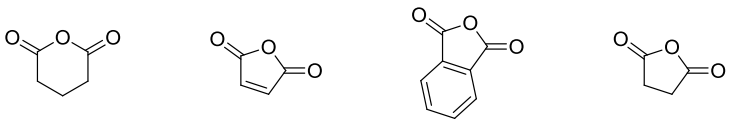


Figure 1.25: Glutaric anhydride, maleic anhydride, phthalic anhydride and succinic anhydride

Alkyds are a very popular form of coating as a result to their low cost, good film forming properties, high viscosity, good drying and hardness properties and their ability to blend well with other paint additives.[105,124] The main problem surrounding the use of this class of coating is the use of high percentages of organic solvents; because of this, research has looked into high-solid content (e.g lowering of the percentage of organic solvents) and water dispersible alkyd resins. In order to be able to reduce the amount of organic solvent in these resins the viscosity of the polymer itself has to be lower, thus a lower weight or smaller weight distribution needs to be

attained. Highly branched alkyds have shown promising results with regards to this, lowering the viscosity and keeping the properties indicative of good quality coatings.[125] Water soluble alkyds have also been investigated. Aigbodion *et al*[126] investigated the incorporation of the alkyd resin of maleinized rubber seed oil into an alkyd emulsion. Various samples of maleinized rubber seed oil were synthesised with differing amounts of maleic anhydride incorporated.

Alkyd resins were then prepared using the modified rubber seed oil along with phthalic anhydride, maleic anhydride and glycerol. Initial reaction with glycerol was followed by polycondensation of the resulting alcohols with the anhydrides to produce the polymer. Once acquired the alkyd was mixed with the previously maleinized rubber seed oil and water and then stirred vigorously to give an emulsion. Testing indicated that viable films could be cast which were resistant to water and acid.[126]

Research on alkyd emulsions has also been reported by Wang *et al*, this time looking at tung oil modified soybean alkyds.[127] Again the alkyd was prepared subsequent to emulsification. In this example, soybean and tung oil were reacted with **(45)**, following the alcoholysis, isophthalic acid was added followed by methanol to afford the alkyd resins, (Figure 1.26). The subsequent emulsion was then prepared using *N*,*N*-dimethyl ethanolamine, 2-butoxyethanol and the alkyd resin along with deionised water mixing at a high speed for at least 2 hours. If the ratio of tung oil to soybean was increased the droplet size of the final emulsions rose quite substantially with an increase from 172 to 771 nm. The emulsions were tested for stability over time up to a temperature of 50 °C where the droplet sizes of all samples were considerably reduced with a final droplet size of 40 to 56 nm. In general the film

forming properties were shown to be good, with the increase in tung oil improving the properties slightly.

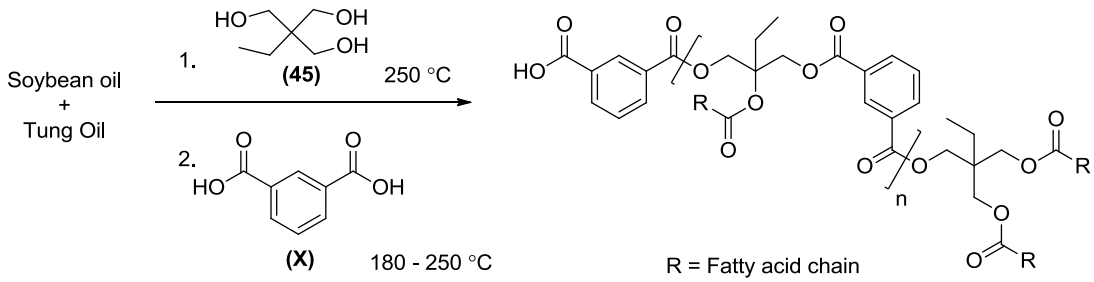


Figure 1.26 Synthesis of alkyds from soybean and tung oil

1.4.4. Acrylics in Latex-Based Coatings

Acrylic monomers have long since been incorporated into water-borne binders, usually *via* the emulsion polymerisation method to produce latex-based paints. Until recently these mononomers have been derived from petrochemical sources. One of the earliest latex-based paints utilised a styrene-butadiene copolymer **(46)**, (Figure 1.27).[7] Acrylonitrile, chloroprene, ethyl acrylate, vinyl acetate and vinyl chloride were the next to be investigated for use as monomers within latex production.[4]

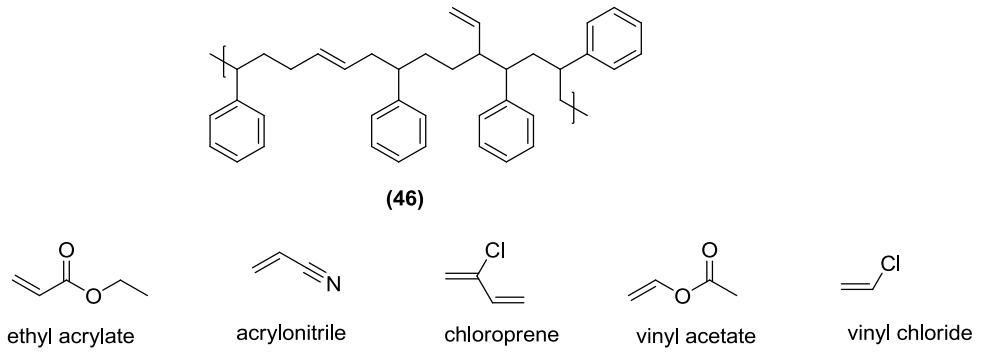


Figure 1.27: Idealised structure of styrene-butadiene copolymer and monomers used within latex based acrylic paints

With consumers and industries alike wanting to use greener products there has been a push towards the incorporation of greener bio-based derivatives. One of the first waterborne coatings was described by Nabuurs *et al*.[128] They investigated an alkyd-acrylic hybrid coating. The idea behind their research was to include the renewable based alkyd resins with the petrochemical based acrylic emulsions to not only create a greener alternative but to also improve upon the disadvantages of both individual systems. One disadvantage of this combined approach included the slow polymerisation of the acrylic portion, but the main advantage was the drying times. In general alkyd resins on their own take a relatively long time to reach a dry non-tacky state. Acrylic dispersions reach this state much quicker; this advantage is translated into the hybrid system.

Van Hamersveld *et al* also investigated hybrid latexes as binders for waterborne systems.[129] The research showed successful stable film forming solids prepared using long oil alkyds and ethyl methacrylate in mini-emulsion polymerisation. On comparison of these hybrid coatings with blended coatings, faster drying times were observed with the hybrid along with increased hardness and clearer films with a broad composition range.

Not only have triglycerides been incorporated into coatings, but they have also started to be used in other polymer applications. There are many types of polymers that can be prepared from renewable oils including; polyesters, polyurethanes (see chapter 4), polyamides, and epoxy resins.[130-132] The work in this thesis does not concern the synthesis of polyesters and polyamides and so they will not be discussed any further, however we will prepare a range of epoxidised vegetable oil based monomers and so a brief discussion of renewable epoxides in resin formation is included.

1.4.5 Epoxy Resins

Epoxy resins have become extremely popular as all-purpose adhesives.[133] In general these adhesives consist of two reactive parts, one which has the epoxide containing component, and the other which contains a 'hardener'; this is normally a polyamine. When the two components are mixed together the epoxide is ring-opened by the nucleophilic amine causing a strong highly cross-linked polymer, this is known as curing. A typical epoxy resin is afforded through the reaction of bisphenol-A and epichlorohydrin (Figure 1.28), along with an amine hardener, commonly triethylenetetramine which can react with epoxy end groups giving a highly cross-linked network.

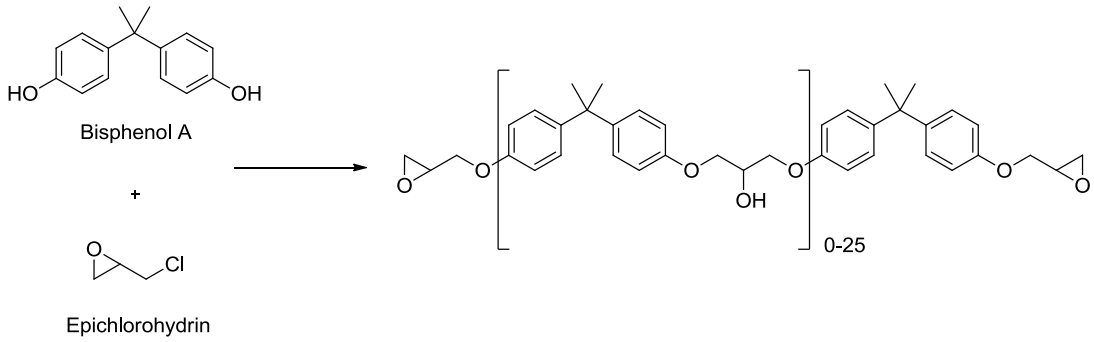
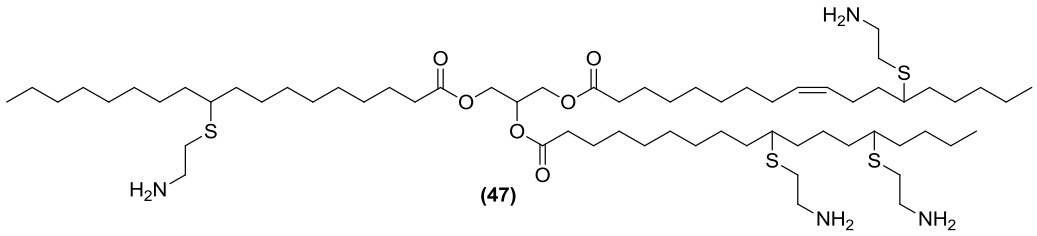


Figure 1.28: Synthesis of epoxy prepolymer resin

Stemmelen *et al* investigated the synthesis of vegetable oil derived epoxy resins, with both the epoxy and the hardener being derived from biomass.[134] The first step was to aminate the triglyceride using cysteamine hydrochloride at RT under UV light which was used to promote the reaction using the photoinitiator 2,2-dimethoxy-2-phenylacetophenone to give **(47),** (Figure 1.29).

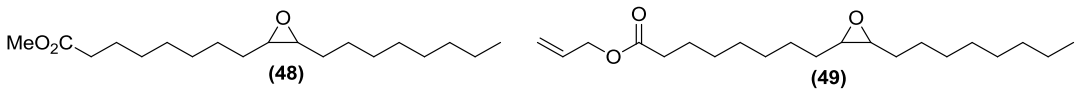


(47)

Figure 1.29: Aminated grapeseed oil (47)

To test the aminated grapeseed oil monomer as a hardener in epoxy resins, stoichiometric amounts of this and epoxidised linseed oil were mixed together at room temperature to give a cured polymer, with a glass transition temperature of -38 °C.

Zhu *et al* successfully developed epoxidised soy-based monomers for use within epoxy resin systems.[135] Two methods were investigated, transesterification with either methanol or allyl alcohol was carried out followed by epoxidation using mCPBA to give epoxy esters **(48)** and **(49)** respectively, (Figure 1.30).



(48) (49)

Figure 1.30: Epoxidised methyl soyate (48) and epoxidised allyl soyate (49).

1.5 Summary

With the recent EU legislations into the use of VOCs and the current shift into the use of greener more environmentally friendly polymers and coatings, extensive research has been made into the use of vegetable oils as raw materials for a variety of different applications. Vegetable oils have been used historically in a number of

industries, specifically paints, prior to the discovery of crude oil. The chemistry of trigylcerides is mainly focussed around reactions at unsaturated points in the side chains and by trasnsesterification or amidation of the ester groups. Due to this and the versatility of triglycerides they represent a good starting point for the advancement of greener chemicals. One of the more recent applications of triglycerides is in waterborne technology.[136,137]

1.6 Aims of Thesis.

The aims of this thesis are to develop a range of *liquid* fatty acid and triglyceride monomers suitable for incorporation into waterborne dispersions *via* mini-emulsion polymerisation for paint applications at room temperature. The study will involve characterisation of the monomer mixtures rigorously by Nuclear Magnetic Resonance (NMR), mass spectrometry (ESI MS), gel permeation chromatography (GPC), thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) to understand their composition. A main focus will be the preparation of coatings from novel monomers that do not undergo yellowing or undergo yellowing slowly with time. Yellowing is thought to occur due to radical autoxidation of residual unsaturation in polymer films, but an approach where these alkenes removed by reduction prior to polymerisation is likely to lead to high melting point monomers which would be too viscous or solids at room temperature due to increased van der Waals interactions between side-chains. Instead an approach where residual alkenes are epoxidised will be investigated. This will retain the ‘kink’ found in unsaturated fatty acid derivatives leading to similar structures to unsaturated oils but with less yellowing potential. A range of triglyceride feedstocks will be investigated

including commercially available rapeseed and soybean oils along with cocoa butter (a waste product from the confectionary industry) to determine the effect of unsaturation and epoxidation levels in paint applications. Latexes will be prepared from novel monomers and their particle sizes measured. Polymers will be analysed by GPC and films will be cast to measure the minimum film formation temperature (MFFT) and hardness.

Finally, a selection of feedstocks prepared in the course of this work will be evaluated as monomers in polyurethane formation with MDI. Their physical and mechanical properties will be measured and these compared to polyurethanes prepared by blending the same monomers and conventional petrochemical derived polyols.

Chapter 2: Synthesis of Novel Biomonomers.

This chapter will concentrate on the synthesis of various 'biomonomers' all derived from triglycerides. A range of methacrylate, styrene, maleate and simple alkene derivatives, suitable for application in latex (defined in Chapter 3) formation are described, as well as their thermal properties.

2.1 Composition of Triglycerides

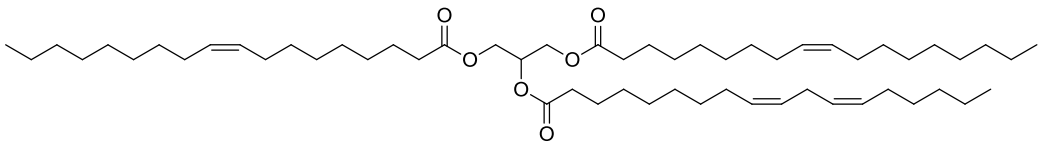


Figure 2.1: Example triglyceride

We chose to investigate the use of readily available renewable oils as our starting materials to make a range of new biomonomers for use in paint binders. We chose triglycerides that were either commercially available in multi-tonne quantities (e.g. soybean), or waste triglycerides available from large scale industrial processes (e.g. cocoa butter). Before chemical modification can be attempted it is important to determine the chemical make-up of each oil and assess the levels of unsaturation and polyunsaturation in the fatty acid chains. The compositions of the various trigylcerides used in this study were deduced using Fatty Acid Methyl Ester (FAME) analysis. This involved transesterification of each oil with MeOH to produce the corresponding methyl esters, which could then be analysed using gas

chromatography, (Table 2.1).[138] Note: Only data for the five most abundant fatty acid methyl esters are shown, consequently percentages may not add up to 100%.

Oil (# alkenes per molecule)	**Palmitic (16:0) %**	**Stearic (18:0) %**	**Oleic (18:1) %**	**Linoleic (18:2) %**	**Linolenic (18:3) %**
Cocoa Butter (1)	25.8	37.9	32.2	2.9	0.9
Rapeseed (3)	5.2	1.5	60.5	19.8	10.5
Soybean (4)	11.4	4.0	23.1	54.2	7.3
Sunflower (5)	6.1	3.1	36.8	49.8	2.9
HO* Sunflower (3)	4.0	2.9	83.8	8.5	-

*** HO = High Oleic**

Table 2.1: Fatty acid composition of selected vegetable oils and fats[4] (Oils supplied by Akzo Nobel, and cocoa butter supplied by Regenesis)

From the five oils analysed, we chose three (cocoa butter, rapeseed oil and soybean oil) to be investigated further. They were chosen because they differ extensively in their chain lengths (Table 2.1) as well as their degree of unsaturation and thus their physical properties. Cocoa butter contains significantly more saturated C16 chains than either rapeseed or soybean oil. Rapeseed and soybean oils are both liquid at room temperature and more similar to each other in their physical properties than cocoa butter, which is a waxy solid.

As discussed before, triglycerides and their derivatives have been reported as monomers in paints before, specifically alkyd coatings.[139] It has been postulated[8] that the extensive yellowing in these paints over time could be due to the abundance of

residual unsaturation in the fatty acid chains. This hypothesis was another reason for choosing a selection of triglycerides that differ in terms of their unsaturation and to determine what effect this might have on the stability and yellowing of the polymer films.

Cocoa butter was chosen not only for its lack of unsaturation but also because it is a waste product from the chocolate manufacturing industry. The waste has found a limited market in the cosmetics and other specialised industries.

2.2 Approaches to Triglyceride and Fatty Acid Derivatization.

Monomers suitable for the incorporation into latexes require activated groups (e.g. methacrylates and styrenes) to be present for efficient polymerisation. Two approaches to insert such functionality were identified, (Figure 2.2). The first delivers functionality incorporated into triglycerides themselves **(50)**, while the second provides functionality into lower molecular weight fatty acid derivatives **(51)**. Both approaches utilise triglycerides as the ultimate starting materials.

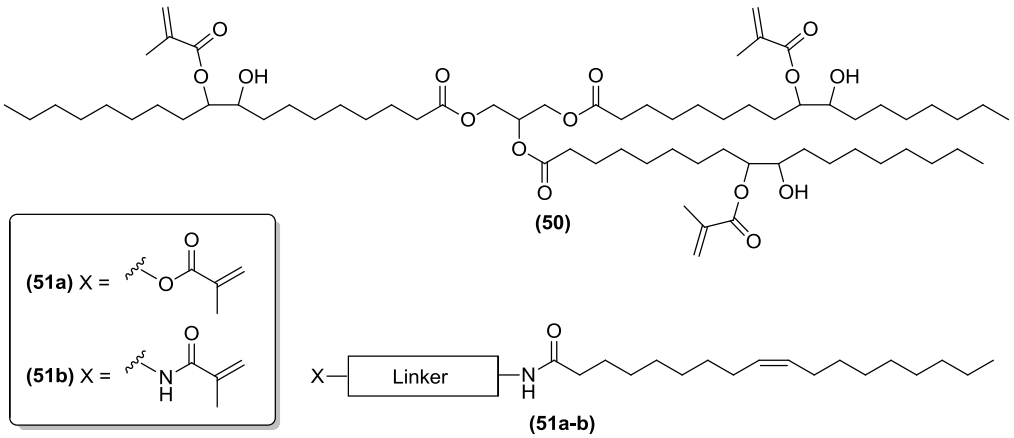


Figure 2.2: Functionalised triglyceride and functionalised fatty acid with methacrylate and methacryloyl-amide groups repectively

2.2.1 Approach 1. Triglyceride Methacrylates a 'Conventional' Approach.

Functionalised triglycerides of type **(50)** have been used in the synthesis of polyurethanes.[140] Molecules of this type can be prepared in two ways (Figure 2.3). The first approach involves epoxidation of the unsaturated groups in any chosen oil, followed by ring opening with appropriately functionalised nucleophiles such as acrylic acid (pathway A).[99] This furnishes one acyl group per epoxide **(50)**. Alternatively, ring opening of the epoxides **(52)** with water furnishes diols **(53)** which can then be further functionalised by acid chlorides to give similar functionalised systems **(50)** but with greater control of the level of acylation (pathway B). Both approaches could furnish monomers carrying multiple polymerisable sites within each molecule, leading to highly cross-linked polymers. One disadvantage would be that due to the statistical nature of the composition of the triglycerides each molecule in any given monomer mixture may have a different pattern and number of polymerisable groups.

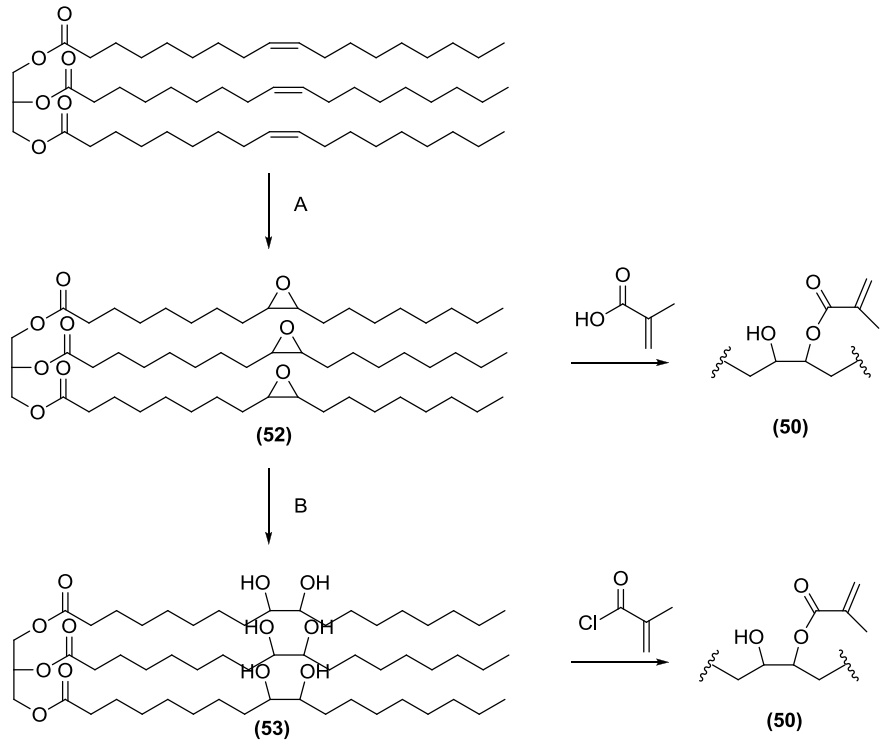


Figure 2.3: Pathways A and B for approach 1

2.2.2 Approach 2.

The second approach we identified was to prepare fatty acid derivatives, with (or without) epoxide functionality, that incorporated various linker systems containing a polymerisable group.

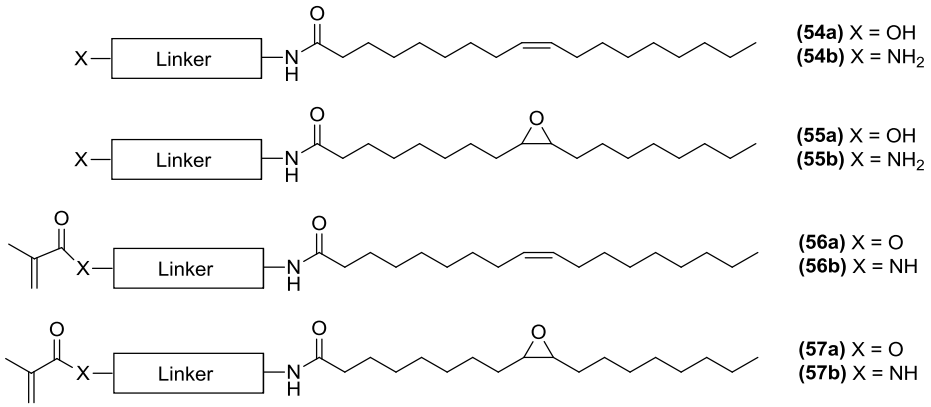
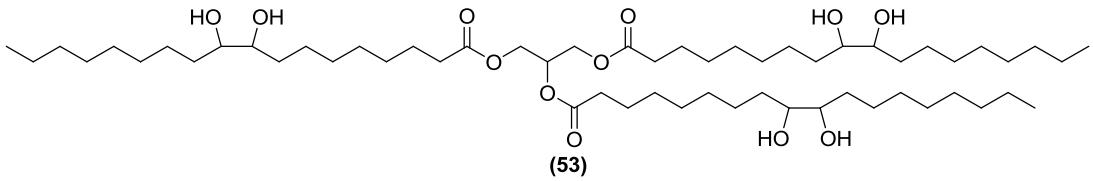


Figure 2.4: Functionalised fatty amide monomers with or without epoxide groups

In this approach we would initially prepare fatty acid derivatives **(54a-b)** and **(55a-b)** containing a terminal heteroatom (X) by transesterification or amidation of triglycerides. We would vary the type and length of the linking chain, as well the heteroatoms (X) present. Functionalisation of these linkers with polymerisable groups (e.g. by methacrylate), would deliver renewable monomers with only one or two polymerisable entities **(56a-b)** and **(57a-b)** respectively. The advantage of approach 2, compared to approach 1 detailed above, is that each monomer molecule would have the same number of polymerisable groups, (irrespective of type of fatty acid). The addition of epoxy groups to these chains could potentially serve a triple purpose of a) removing unsaturation and lowering yellowing, b) serving as a point of attachment for further functionalisation or cross-linking if necessary, and c) retaining the overall 'kinked' shape of the C-18 chains found with the *cis*-alkenes providing comparable packing and melting properties to the parent olefin.

2.3. Application of Approach 1.

The disadvantages of this approach were outlined in section 2.2.1. As a consequence, we decided to prepare only one monomer using this approach. Hence, rapeseed oil was initially epoxidised using the Venturello procedure[141] and then ring-opened *in situ* by water and orthophosphoric acid to give the rapeseed polyol **(53)**.[51]



(53)

This involved initial preparation of a tungsten catalyst by the reaction of W metal, phosphoric acid and hydrogen peroxide at 50 ˚C for 45 min followed by addition of

the catalyst to an emulsion consisting of a mixture of rapeseed oil, water, hydrogen peroxide, orthophosphoric acid and a phase transfer catalyst (adogen 464) at 100˚C. After rapid stirring for 6 hrs at this temperature the two phases were separated and the diol isolated. Esterification of the diol by reaction with 1.1 eq of methacryloyl chloride and the base Et_3N furnished the functionalised monomer **(50)** in 79% yield (with on average one polymerisable group per molecule). The thermal properties of this monomer **(50)** were explored by TGA and compared to the parent rapeseed oil (RSO) and rapeseed polyol **(53)**. The melting point and Tg were also measured by DSC.

TGA analysis indicates that hydroxylation of rapeseed oil (RSO) lowers the thermal stability of the derivative **(53)** to below 400 ˚C and the second 'kink' in the curve for **(53)** observed around 80% mass loss indicates two decomposition pathways. The methacrylated triglyceride **(50)** has even less thermal stability, starting to decompose around 200 ˚C and the TGA shows that the monomer appears to degrade in multiple steps, although this happens over a small temperature range. This is could be due to decomposition by elimination of methacrylic acid being more favourable than the elimination of water and that a mixture of products was formed during addition of the methacrylate group to the hydroxylated triglyceride **(53)** giving rise to mono-addition or di-addition of methacrylates.

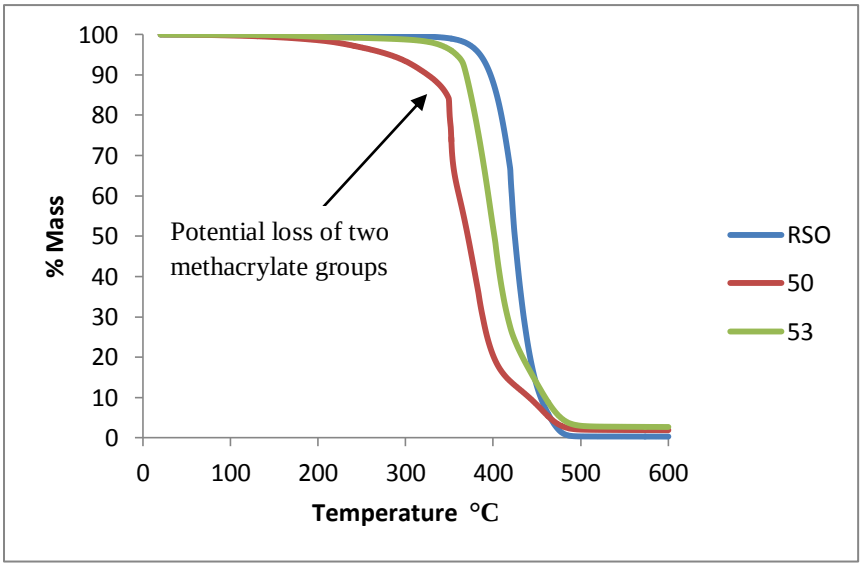


Figure 2.5: Graph showing thermal breakdown of rapeseed oil (RSO), rapeseed polyol (53) and rapeseed methacrylate (50)

Functionality	Tg (°C)	M.P. (°C)
Rapeseed methacrylate **(50)**	-38	-8

Table 2.2: Melting point and glass transition temperatures of functionalised triglyceride

2.4 Application of Approach Two

The main focus of this project involved the synthesis of smaller fatty acid based amides (Figure 2.6) as starting blocks for further functionalisation (**(60)** linker = C_n = C-2, C-4, C-6). Previous work by the Thames group in Mississippi[137] had synthesised a number of methacrylate monomers **(58)** and **(59)** derived from **(30)** itself derived from triglycerides and diethanolamine for use in waterborne systems (Figure 2.6). We wanted to use this approach to make more hydrolytically stable amides **(60a-c**), (Figure 2.6) derived from diamines **(54b/55b)**, (Figure 2.4).

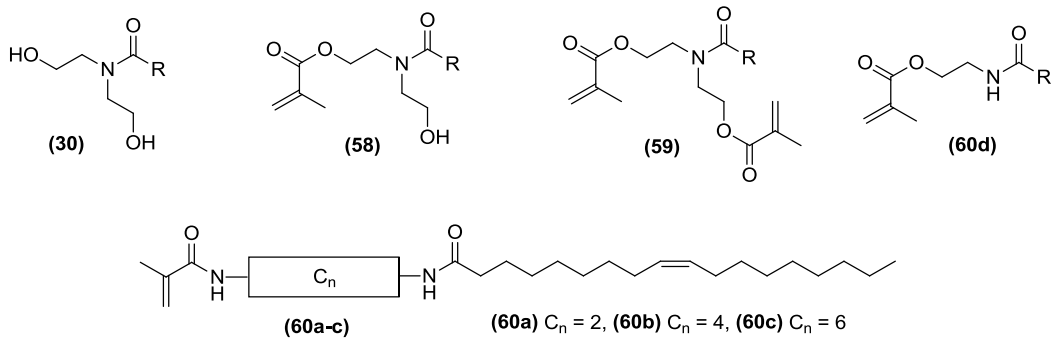


Figure 2.6: Fatty acid based amide methacrylates using linkers of various chain length

This also would allow us to compare the effect of replacing the ester functionalised methacrylates of the Thames group **(58/59)** with amides **(60a-c)**. Consequently, we also prepared the ethanolamine **(60d)** and diethanolamine **(58/59)** derivatives as control monomers. All the methacrylate monomers (with the exception of that derived from diethanolamine **(30)**) contain one polymerisable methacrylate group, unlike the rapeseed methacrylate derivative **(50)**, where control in the addition of the methacrylate group was difficult due to the varying amount of hydroxyl groups present in the rapeseed polyol **(53)**. Consequently, our first targets were the amides **(30)** and **(61a-d)** derived from rapeseed [RS**(30)**, RS**(61a-d)**], soybean [SB**(30)**, SB**(61a-d)**] and cocoa butter [CB**(30)**, CB**(61a-d)**]. We also prepared **(30)** derived from triolein to help in assigning ^{1}H NMR spectra.

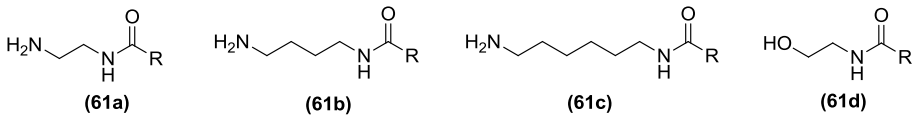


Figure 2.7: Fatty acid based amides using linkers of various chain length

2.4.1 Synthesis of Rapeseed, Soybean, and Cocoa Butter Amides

The amides **(30)** and **(61a-d)** were prepared by reacting the appropriate triglyceride with a diamine or ethanolamine and sodium methoxide in an aminolysis reaction (Figure 2.8).

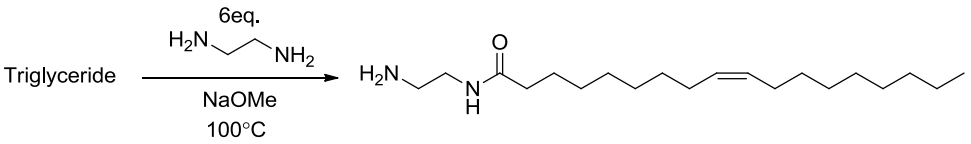


Figure 2.8: Aminolysis of a triglyceride with ethylenediamine[142]

Rapeseed derivatives RS**(30)** and RS**(61d)** were prepared by the previously published literature method.[137] Hence, rapeseed oil was reacted with 3 equivalents of ethanolamine or diethanolamine and NaOMe at 60 ˚C for 4 h to give RS**(30)** and RS**(61d)** in 97% and 89% yields respectively, (Table 2.3). However, upon application of this protocol to the synthesis of RS**(61a**) derived from ethylenediamine **(62a)** a mixture of products was formed.

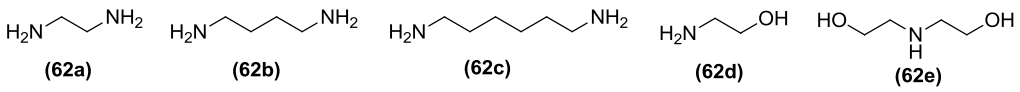


Figure 2.9: Ethanolamines and diamines used in aminolysis reactions

Due to the symmetrical nature of the diamine **(62a)** both the desired monoamide RS**(61a)** and the diamide RS**(63a)**, where a fatty chain had added on to each end of the amine, were produced in a statistical mixture. As a consequence, a significant amount of mono RS**(64)** and diglycerides RS**(65)** were also isolated, (Figure 2.10).

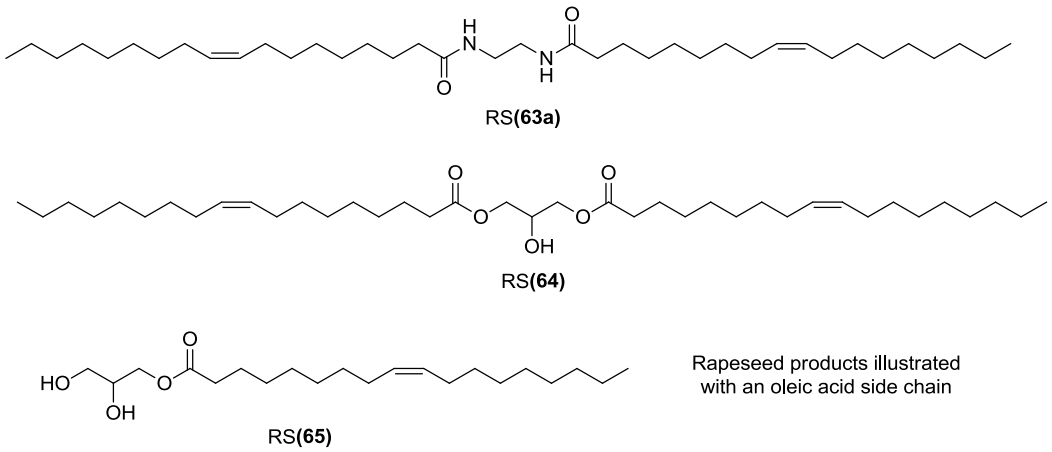


Figure 2.10: Example of diamide with two oleic chains

By increasing the amount of diamine used from 3 equivalents to 6 equivalents it was possible to improve the yield of the desired monoamide RS**(61a)** at the expense of the diamide RS(**63a)**. A typical procedure involved reacting 6 equivalents of ethylenediamine with rapeseed oil and sodium methoxide for 6 h at 60 °C, without the aid of a solvent. The diamide could be easily removed from the crude reaction mixture by eluting the mixture through a short silica plug. The undesired diamide RS**(63a)** was eluted from the column followed by the desired monoamide RS**(61a)**. We then extended the procedure to all the diamine and ethanolamine linkers **(62a-e)** with all three triglyceride starting materials (rapeseed, soybean and cocoa butter). Problems were encountered during the work-up stages of all of the reactions. On addition of water to remove any glycerol and unreacted amine, an emulsion was observed, making separation extremely difficult. The addition of salt water did not help; however heating the emulsion did facilitate separation. Breaking of the emulsions was more challenging for the cocoa butter derived amides it being necessary to leave them for extended periods of time for satisfactory separation (24 h). It is not surprising that the monomers form emulsions easily, as they are typical

surfactants (having a hydrophilic head and a hydrophobic tail). The reactions were initially carried out on a small scale (<10g) and then a large scale 200-500g.

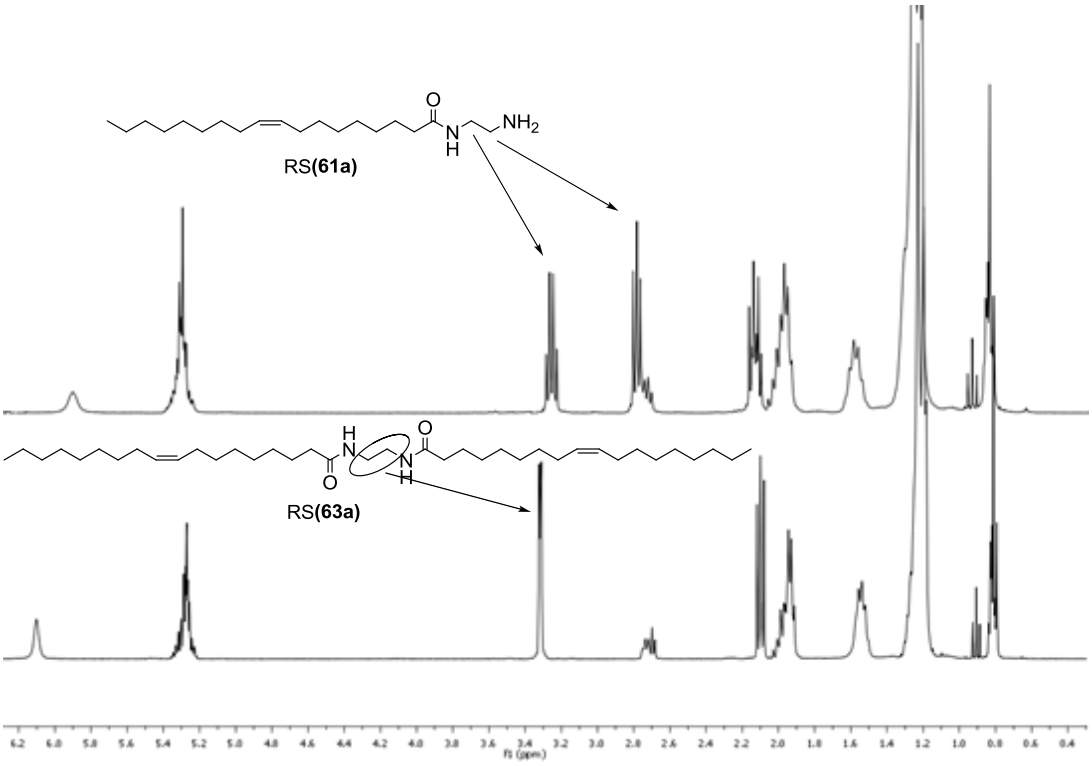


Figure 2.11: 400MHz ^{1}H NMR spectra showing mono- RS(61a) (top) and di- RS(63a) (bottom) amides synthesised with rapeseed oil (RS) and ethylenediamine (62a).

Entry	Oil	% yield				
		(61a)	(61b)	(61c)	(61d)	(30)
1	Rapeseed (RS)	74	82	86	97	89
2	Cocoa butter (CB)	56	75	80	82	91
3	Soybean (SB)	81	91	82	89	90
4	Triolein (TO)	-	-	-	-	93

Table 2.3: Percentage yields of mono aminolysis products.

Over the course of the reaction the physical appearance of the initial triglyceride oils changed quite substantially, this was dependent upon the amine used. Powdery solids

were observed with the use of the diamines **(62a-c)**, waxy solids with ethanolamine **(62d)** and viscous oils with diethanolamine **(62e)**. Presumably the increased hydrogen bonding found in **(62a-c)** is responsible for this behaviour. As previously mentioned, because the starting triglycerides contain a mixture of different fatty acid components (Table 2.1), the amide product sets **(61a-d)** and **(30)** are also mixtures. ^{1}H nuclear magnetic resonance (400 MHz NMR) was not satisfactory in fully analysing product sets, instead electrospray mass spectrometry was used to characterise the different chains. Figure 2.12 shows the mass spectrum for the rapeseed amide RS**(61a)** synthesised with rapeseed oil and ethylenediamine (Entry 1 Table 2.3). Peaks were observed for fatty chains with 0, 1, 2 and 3 double bonds, corresponding to stearic, oleic, linoleic and linolenic acid chains respectively. In fact the relative proportions in the mass spectrum parallel those found in the FAME analysis (oleic > linoleic > linolenic > stearic)

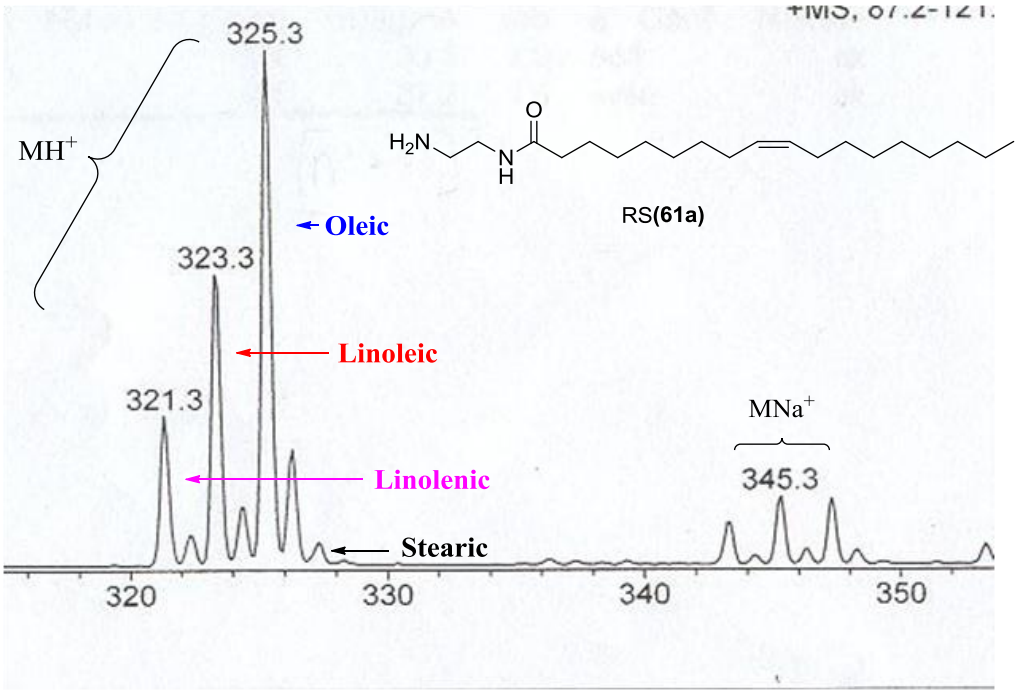


Figure 2.12: Electrospray mass spectrum showing RS(61a). Masses due to oleic, linoleic, linolenic and stearic chains can be clearly seen.

2.4.2 Functionalisation of Amine/Hydroxyl End Groups

In order to be incorporated into a polymer latex we next needed to attach appropriate functionality to the free amine or alcohol groups of the fatty acid amide derivatives. In mini-emulsion polymerisation, it is normal to have vinyl (styryl), or acrylate groups as the reactive components of the monomer group.

2.4.2.1 Methacryloylation

With 16 amine and alcohol terminated amides in hand, attention was turned to their functionalization to give the methacryloyl derivatives [RS**(60a-d)**, RS**(58/59)**, SB**(60a-d)**, SB**(58/59)**, CB**(60a-d)**, CB**(58/59)**, and TO**(58/59)**].

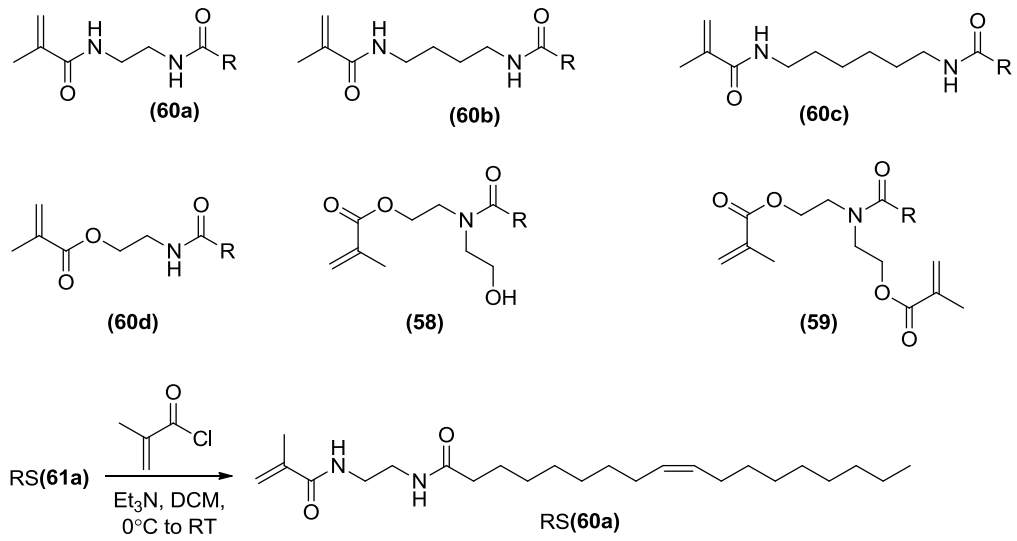


Figure 2.13: Target methacrylate derivatives

Reaction was accomplished by reacting the amine and alcohol derivatives [RS**(61a-d)**, RS**(30)**, SB**(61a-d)**, SB**(30)**, CB**(61a-d)**, CB**(30)**, and TO**(30)**] in DCM at 0 °C, with 1-2 equivalents of Et_3N followed by the drop-wise addition of methacryloyl chloride. The mixtures were stirred and allowed to gradually reach room

temperature. The solubility of the cocoa butter amide derivatives CB**(61a-c)** as well as the ethanolamine derived CB**(61d)** was poor in DCM at 0 °C. For these cases three times the amount of DCM was used as solvent compared to the standard procedure. Figure 2.14 shows the electrospray mass spectrum of the methacryloyl derivative RS**(60a)** derived from rapeseed, again showing the peaks characteristic of the different amounts of unsaturation in the carbon chains.

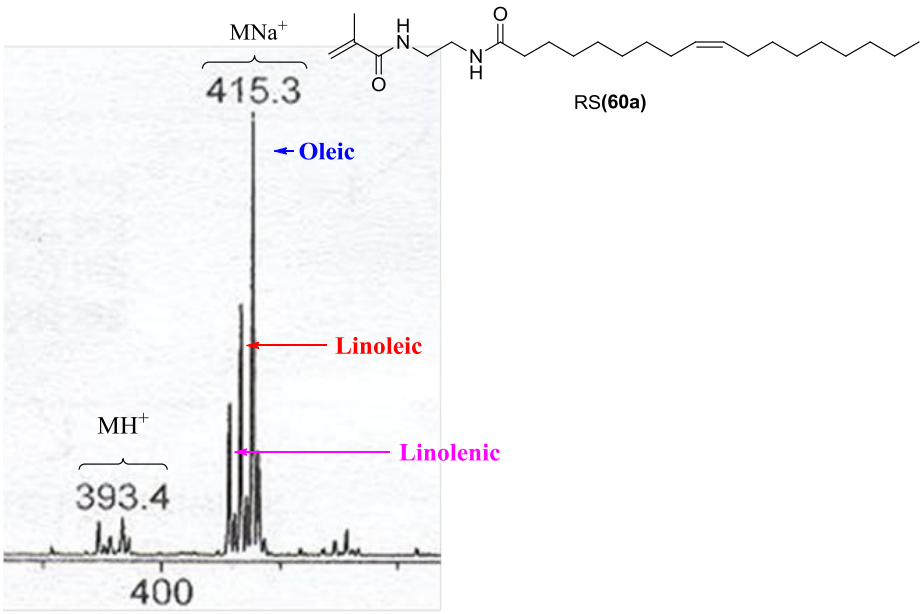


Figure 2.14: Electrospray mass spectrum of RS(60a)

All methacrylated fatty amides where produced in good yields (69%-91%). The process of methacryloylation often affected the physical properties of the compounds. For example, the unfunctionalised ethylenediamine derived amides RS/SB/CB**(61a)** went from being powdery solids to waxy solids upon methacryloylation to give RS/SB/CB**(60a)**. The extent of functionalisation could be followed by ^{1}H NMR. The spectra showed the appearance of peaks between 6.30 and 5.50ppm coupling to a singlet at ~1.95ppm characteristic of the methacrylate

group. In many cases, the crude ^{1}H NMR showed contamination with methacrylic acid. This was easily removed by either column chromatography, or by an additional washing step using saturated $NaHCO_3$ during work-up.

Entry	**Oil**	**% Yield**				
		(60a)	**(60b)**	**(60c)**	**(60d)**	**(58/59)**
1	Rapeseed (RS)	80	91	87	87	89*
2	Cocoa butter (CB)	74	69	67	77	86*
3	Soybean (SB)	90	88	88	85	92*

* - Mixture of mono **(58)** and di-methacrylated **(59)** monomers

Table 2.4 Percentage yields of methacrylated amides

Methacryloylation of the diethanolamine **(62e)** based amides RS/SB/CB**(30)** lead to both mono-**(58)** and di-**(59)** addition of the methacrylate group. On a small scale both compounds could be separated by column chromatography but on larger scales (>20g) no attempt was made to separate them. These monomers (like those derived from rapeseed polyol **(50)**, see section 2.3) present multiple polymerisable sites, which could lead to a highly cross-linked polymers.

2.4.2.2 Addition of a Potential Renewable Styrene Functionality RS(61d).

Styrene is another commonly used monomer functionality used in latexes as seen with styrene-butadiene rubber, which has applications including tyre treads and shoe soles. Recent work within the Clark group has highlighted styrene derivative **(66)** as a potential renewable feedstock derived from the degradation of waste lignin or from vanillin. 2-Methoxy-4-vinylphenol **(66)** can be prepared by decarboxylation of ferulic acid,[143,144] and olefination[52] or organocatalyzed conversion[145] of vanillin, an aromatic compound often used as a flavouring agent. Both vanillin and ferulic acid are commercially available but are both potentially available renewably from the bacterial and chemical degradation of lignin.[146] Lignin is a complex polyphenolic material that is found most commonly in the wood components of plants and trees. It makes up between 10 and 33 % of dried lignocellulose.[147] As a consequence, we briefly explored the feasibility of introducing 2-methoxy-4-vinylphenol **(66)** into one representative fatty acid derived amide, notably the ethanolamine derived fatty acid derivative from rapeseed oil RS**(61d**), (Figure 2.15).

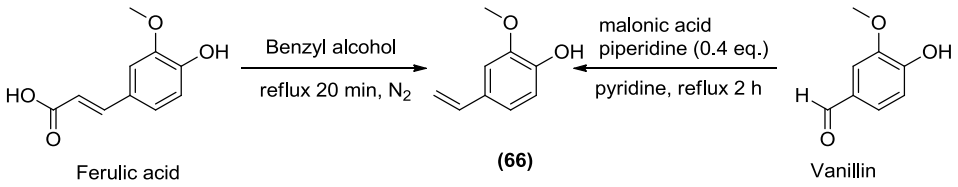


Figure 2.15: Decarboxylation of ferulic acid (A) and olefination of vanillin (B)

The preparation of phenyl ethers from phenols can be accomplished in a number of ways.[148,149] One of the commonest, the Williamson ether synthesis, uses the phenolate and an alkyl halide.[148] Instead of introducing an extra step to turn the alcohol RS(**61d**) into the bromide RS**(67d)** we investigated a direct coupling

protocol using the Mitsunobo reaction, (Figure 2.16). This reaction utilises a simple phosphine, triphenylphosphine and an azodicarboxylate, in this case diisopropyl azodicarboxylate (DIAD) to initiate a coupling to give the desired ether RS**(68d)**.

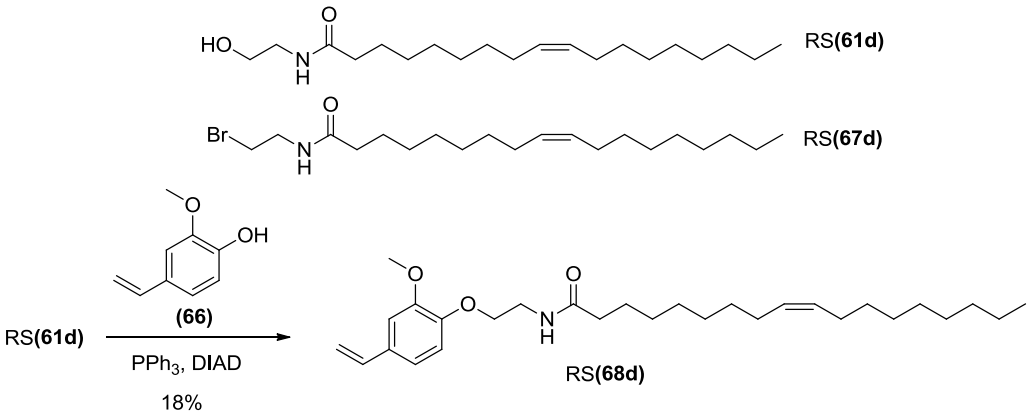


Figure 2.16: Preparation of styrene RS(68d)

Hence, compound RS**(61d)** and 2-methoxy-4-vinylphenol **(66)** were reacted with DIAD and triphenylphosphine at room temperature over 2 hrs to give RS**(68d)** in 18% yield after purification by column chromatography. As the reaction proved particularly low yielding, (which is not ideal for a potential industrial bulk process) and due to only undertaking this step on a small scale, the new monomer was not tested further for its viability within mini-emulsion polymerisation. TGA, (Figure 2.18) shows two different decompositions events, but thermal stability is relatively low with degradation starting to occur at < 200˚C and over a large temperature range (200˚C).

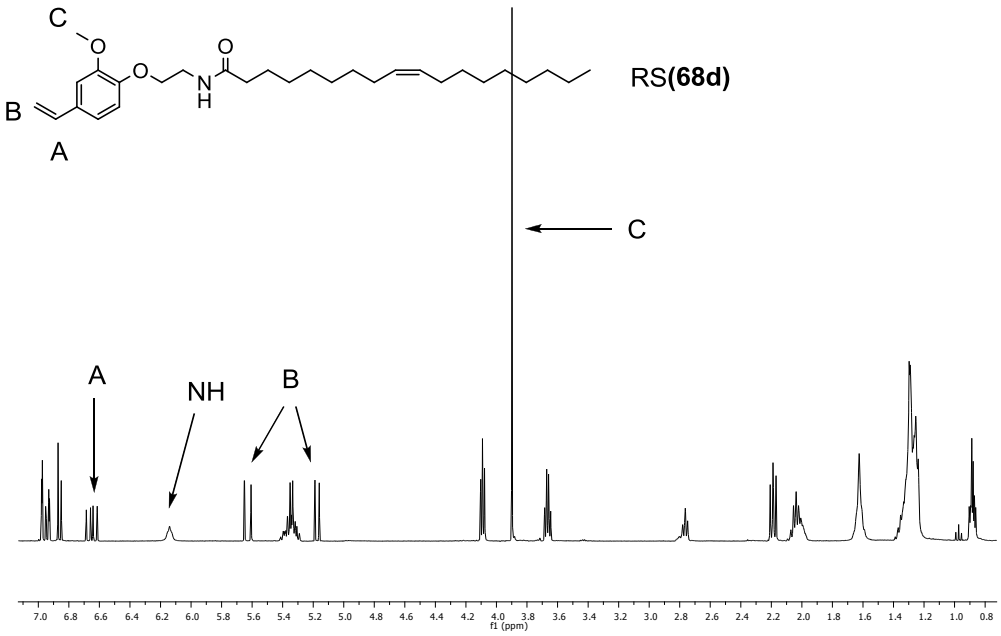


Figure 2.17: ^{1}H 400MHz NMR of novel renewable styrene derivative RS(68d).

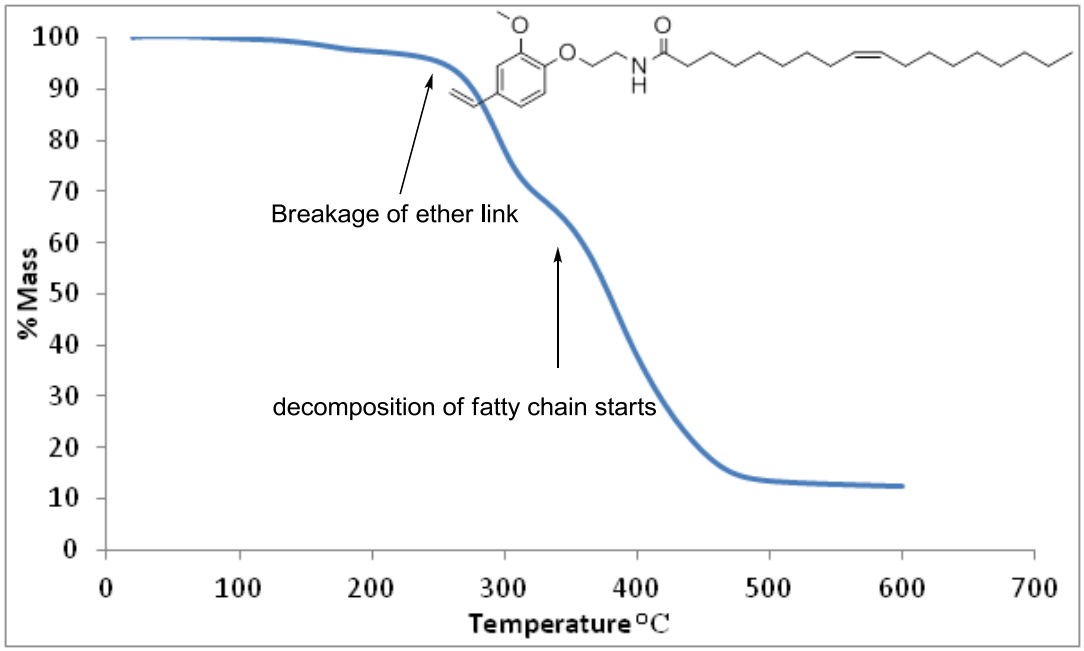


Figure 2.18: Thermal decomposition of styrene derivative RS(68d) showing potential decompositions

2.4.2.3 Maleation

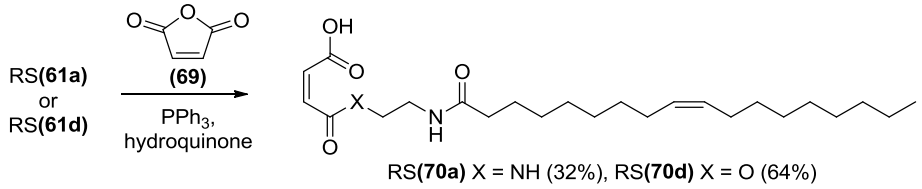


Figure 2.19: Maleation

Maleic functionality is also an important potential unit to incorporate into the renewable monomers for latex formation.[150] As a consequence the maleic functionality was incorporated into the rapeseed derived ethanolamine monomer RS**(60d)** by reacting maleic anhydride **(69)** with the free hydroxyl functionality of the fatty amide. Hence, reaction of RS**(60d)** with **(69)** using triphenylphosphine and hydroquinone at room temperature for 5 hours furnished RS**(70d)** in a 64% yield after column chromatography This reaction was also repeated with the ethylenediamine derived amide RS**(61a)**, however although successful this gave a much lower yield of RS**(70a)** in only 32 %. Unlike the addition of the methacrylate group, these reactions were quite messy and had to be purified *via* flash column chromatography. Due to the difficulty preparing these monomers on a large scale they were not investigated further in latex formation.

2.5 Removal of Residual Alkene Groups: Epoxidation and Partial Epoxidation

As discussed earlier, one of the project aims was to determine if the presence of residual alkene groups left in the fatty acid derivatives side-chains (e.g. RS**(60a)**) were responsible for the yellowing of paint films over time. While it would be possible to remove the alkenes by hydrogenation, it is likely that this would lead to derivatives with unsuitably high melting points due to efficient packing of chains (due to Van der Waals forces). Fats containing unsaturated side-chains are more fluid, with lower melting points because the *cis*-alkenes generate a 'kink' in the side-chains which make packing harder. Consequently, the next step was to remove some or all of the unsaturation from the fatty acid chains, but in such a way that the 'kink' could be partially retained. The method chosen for the removal was to epoxidise the double bonds to give RS**(71a)** (as this proceeds with retention of *cis*-alkene geometry providing *cis*-epoxides).

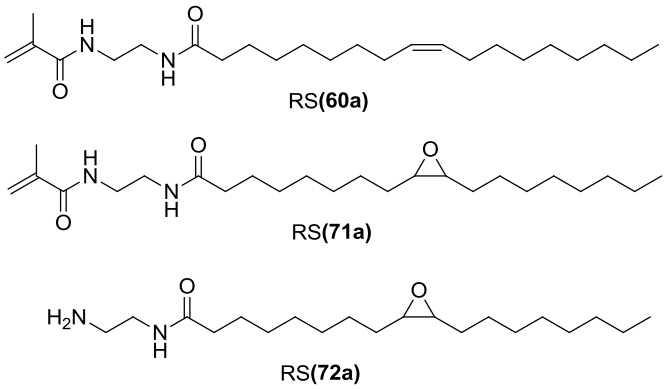


Figure 2.20: Epoxidation of double bond in fatty amide chains

This approach also provides an advantage that further functionalisation of the monomers is possible if necessary or that further cross-linking of films *via* epoxide ring-opening may be accomplished.

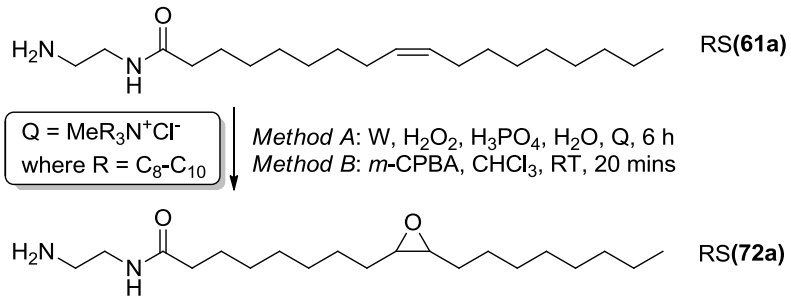


Figure 2.21: Epoxidation of double bond in fatty amide chains

There are many methods available in the literature to epoxidise alkenes[151] but the approach ultimately chosen would need to be carried out on an industrial scale. We investigated, two approaches. The first was that reported earlier, the Venturello reaction, (*Method A,* Figure 2.21). We initially investigated an organic solvent free approach where the reaction was carried out in an emulsion. This involved using the catalyst system described earlier and prepared using tungsten powder dissolved in 30% w/v H_2O_2 and phosphoric acid at 50 °C.[51] This was used in conjunction with the quaternary ammonium salt Adogen 464, which acts as a phase transfer agent. It is believed that the mechanism for this epoxidation follows that of the Jacobsen-Katsuki epoxidation,[152,153] which utilises manganese instead of the tungsten; however the mechanism is not fully understood.[154] Unfortunately all attempts to use this method to epoxidise the amide RS**(61a)** were unsuccessful. The ^{1}H NMR suggested little to no change in the side-chain alkene peak which is found at ~ 5.32ppm, over the course of the reaction this should disappear, to be replaced with a peak at ~ 2.89ppm which represents protons on the epoxide. Previous work[51] has indicated that vigorous stirring is required to allow the transfer of the catalyst between the oil and water phases. However the addition of various organic solvents (ethyl acetate, toluene, DCM) to increase fluidity of the reaction mixture to allow better agitation and the lengthening of the reaction time made no difference to these

findings. It is likely that the presence of amide protons or acidic OH or NH_2 groups retards this type of epoxidation process.

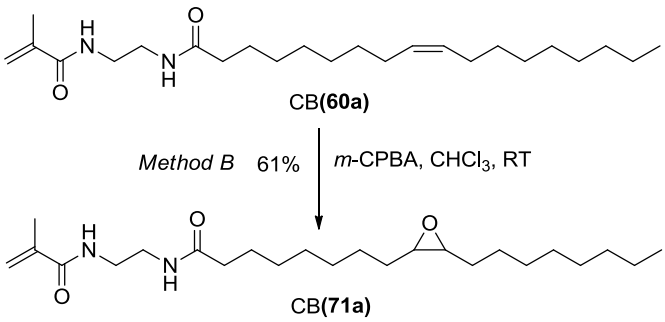


Figure 2.22: Epoxidation of double bond in fatty amide chains

Another approach to epoxidise fatty acid alkenes uses peracids (e.g. $MeCO_3H$). In fact, the Cargill epoxidation process uses $MeCO_3H$ to prepare epoxy soybean oil on an industrial scale.[33] Instead of using peracetic acid we chose to use the commercially available mCPBA. Due to the electron deficient nature of mCPBA, this should preclude competitive epoxidation of any electron poor methacrylate group leading to high selectivities for the side-chain alkene. Hence, reaction of the cocoa butter derived methacryloyl compound CB**(60a)** with 1 equivalent of mCPBA in chloroform at RT for 20 minutes to give the desired epoxide CB**(71a)** in 61% yield, (Figure 2.22). It was possible to follow the reaction by ^{1}H NMR and observe the selective loss of the side-chain alkene peaks at ~ 5.32ppm and the growth of the epoxide peak at ~ 2.89ppm. No reaction at the methacryloyl group (alkene peaks at ~ 5.25ppm and ~ 5.60ppm) was observed, (Figure 2.23). Further characterisation information could be obtained from the electrospray mass spectrum of CB**(71a)**.

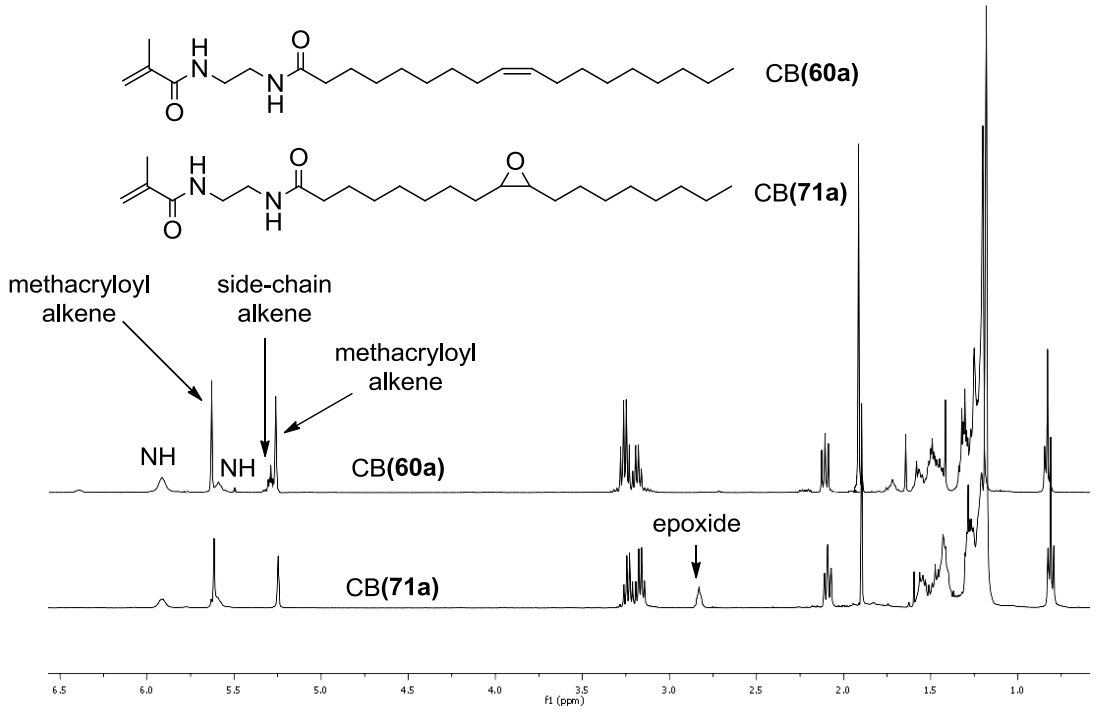


Figure 2.23: ^{1}H NMR comparing epoxidised CB(71a) and unsaturated CB(60a)

The desired peak (MH^+) = 408.3 corresponds to an epoxidised oleic side chain (the main unsaturated fatty acid in cocoa butter, see table 1.1). The other minor peaks at 366.3 and 394.4, correspond to the methacryloyl derived palmitic and stearic side-chains respectively.

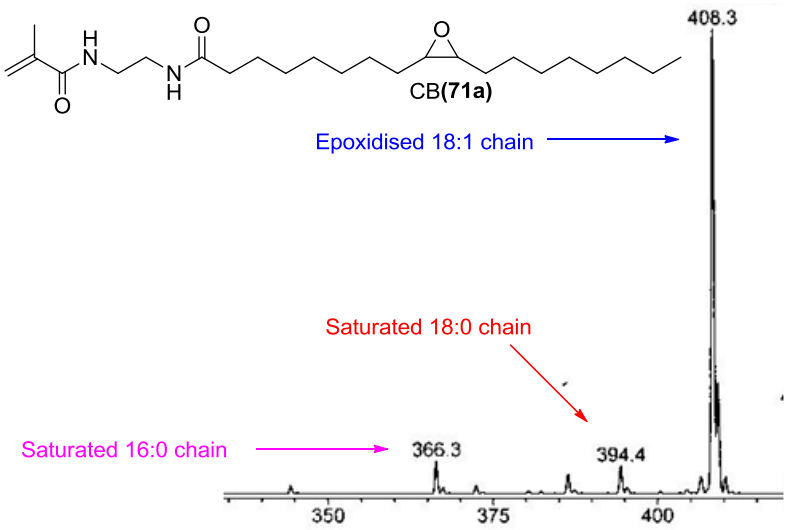


Figure 2.24: Electrospray mass spectrum of CB(71a)

Theoretically there are two routes from the amides **(61)** to methacryloyl derived epoxides **(71)** (pathway A and B). The route already described (pathway A) above involves first adding the methacrylate **(61) → (60)** followed by epoxidation of the residual side-chain double bonds **(60) → (71)**. This route worked well giving high yields. Although the epoxidation was done with mCPBA, the electron deficient nature of the oxidant, precludes competitive epoxidation of the electron poor methacrylate group leading to high selectivities and good yields. The second route involved epoxidising the double bond first **(61) → (72)** and then adding the methacrylate group second **(72) → (71)**, (pathway B). Potential problems with this route involve competitive ring opening of the epoxides during the reaction **(72) → (71)**, (e.g. by chloride or methacrylic acid). However, in order to establish which was the best route for synthesising monomers on a large scale we briefly investigated pathway B.

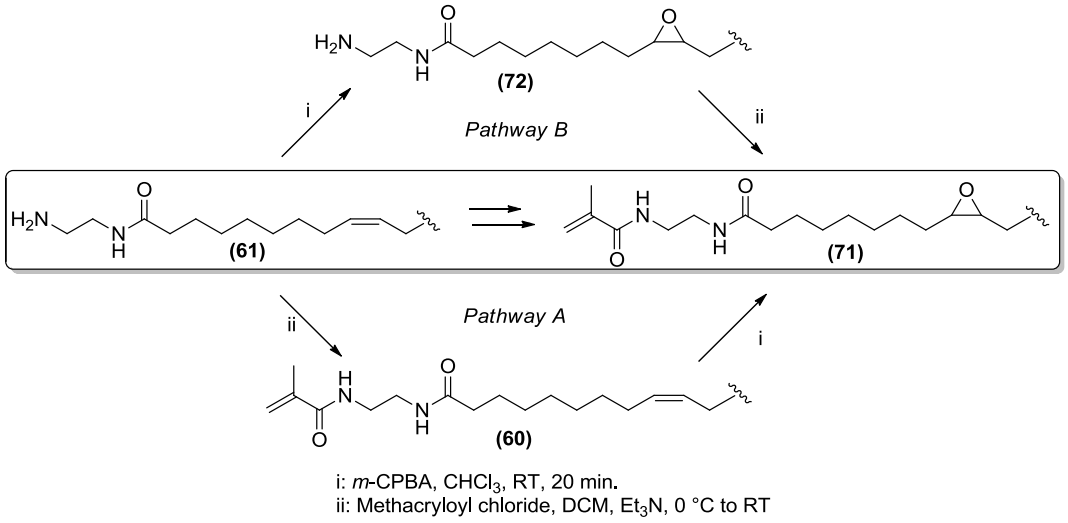


Figure 2.25: Two routes to epoxidised monomer (71)

We investigated pathway B on the amide RS**(30)** derived from rapeseed oil; however, while it was possible to form the desired end product RS**(71)**, the yield was not as high as for pathway A. After chromatography, mass spectrometry (Figure 2.26) evidence indicated a second set of products arising from ring-opening of the epoxide by HCl **RS(73a/b)**. Consequently, we only utilised pathway A in other reactions sequences.

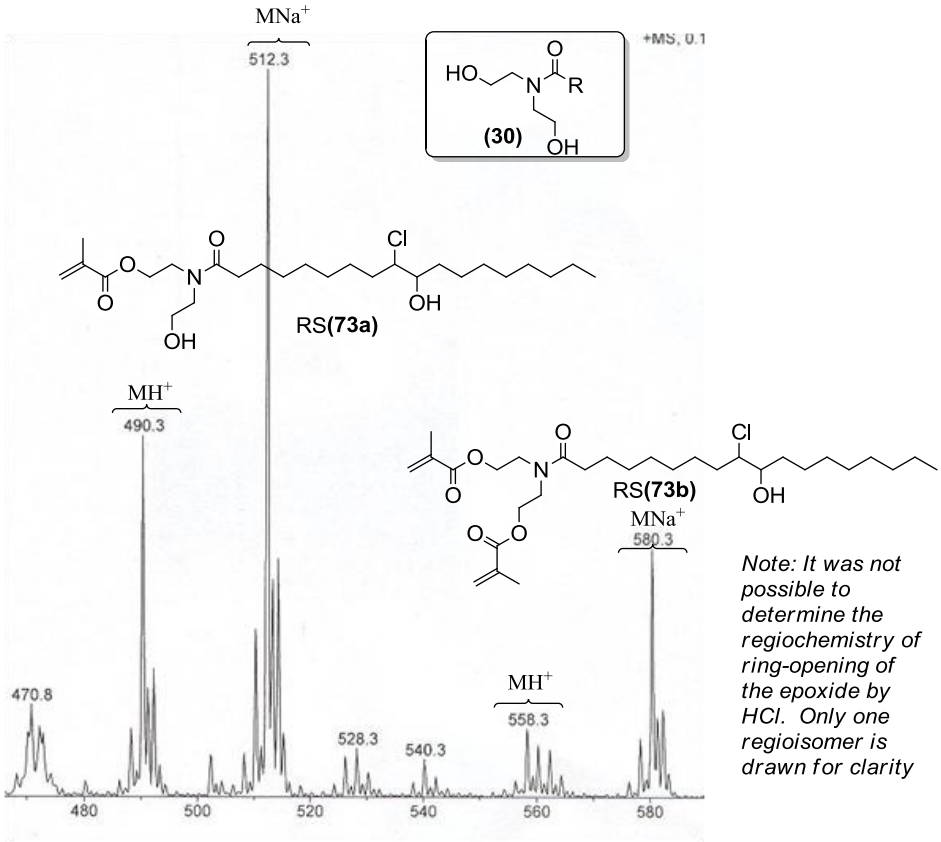


Figure 2.26: Electrospray mass spectrum showing unwanted ring-opened product RS(73a/b).

Due to our original hypothesis that the level of residual alkene groups in latex monomers was important in determining the rate of yellowing of films, we prepared three forms of our final monomers; a) those where all the side-chain alkenes in the monomer mixture were epoxidised **(71a-d)**, (**74**/**75**), b) those where the side-chain

alkenes of the monomer mixture were only partially epoxidised PE**(71a-d)**, PE(**74/75**), and c) those where epoxidation was not carried out **(60a-d)**, **(58/59)**, (Figure 2.27), (Table 2.5).

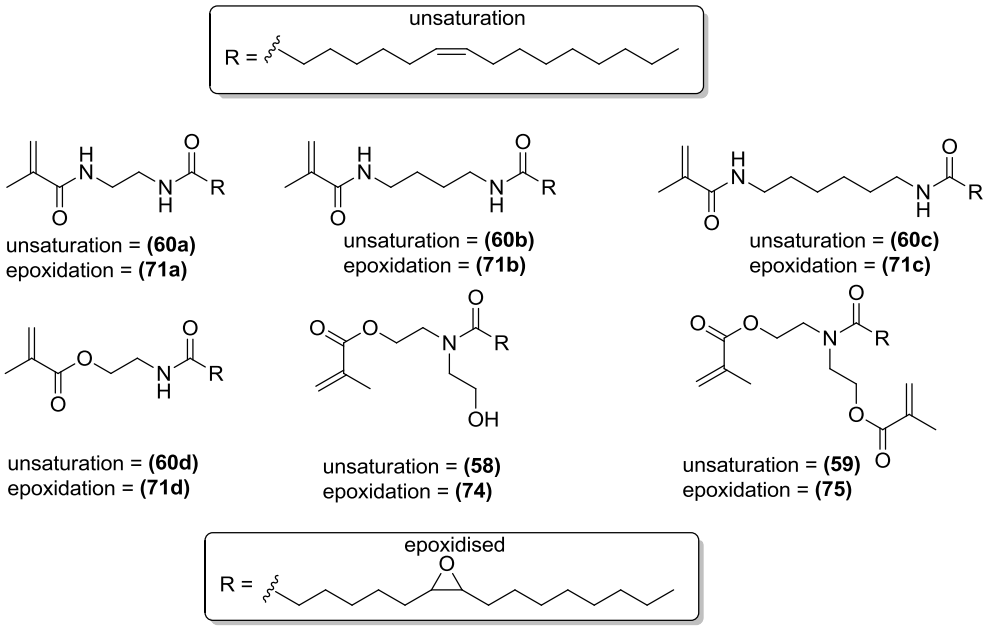


Figure 2.27: Examples of unsaturated (60a-d), (58/59) and epoxidised (71a-d), (74/75) monomers used in this study.

Linker	Rapeseed (RS)		Cocoa butter (CB)		Soybean (SB)	
	Partial	Full	Partial	Full	Partial	Full
(71a)	87	78	65	61	90	89
(71b)	79	79	60	62	89	89
(71c)	81	86	58	60	84	89
(71d)	80	78	-	-	87	83
(74/75)	*	*	-	-	*	-

* - Underwent polymerisation during work-up.
Partital = approx. 50 % of double bonds removed *via* epoxidation, Full = all double bonds removed *via* epoxidiation

Table 2.5: Percentage yields of partially and fully epoxidised monomers

Some difficulty was encountered when trying to isolate the fully and partially epoxidised material derived from the epoxidation of RS**(58/59)**. Removing the diethyl ether at the end of the reaction became problematic as the material was extremely viscous and difficult to remove from the apparatus. On leaving the monomer, over twelve hours under atmospheric conditions to remove the last traces of solvent, a very hard resin polymer was formed. It is likely that the free primary hydroxyl group present in the **(58)** component of the mixture either initiated a ring opening polymerisation of the epoxide or an addition polymerisation of the methacrylate groups. In the latter case cross-linking could occur *via* component **(59)** leading to the observed material. The material was analysed by TGA (Figure 2.28) which indicated a relatively stable material up to 300 ˚C. Degradation then takes place over quite a wide temperature range 300-460 ˚C. Due to this undesired outcome the epoxidation of derivatives **(58/59)** of rapeseed (RS), cocoa butter (CB), and soybean (SB) oils were not attempted.

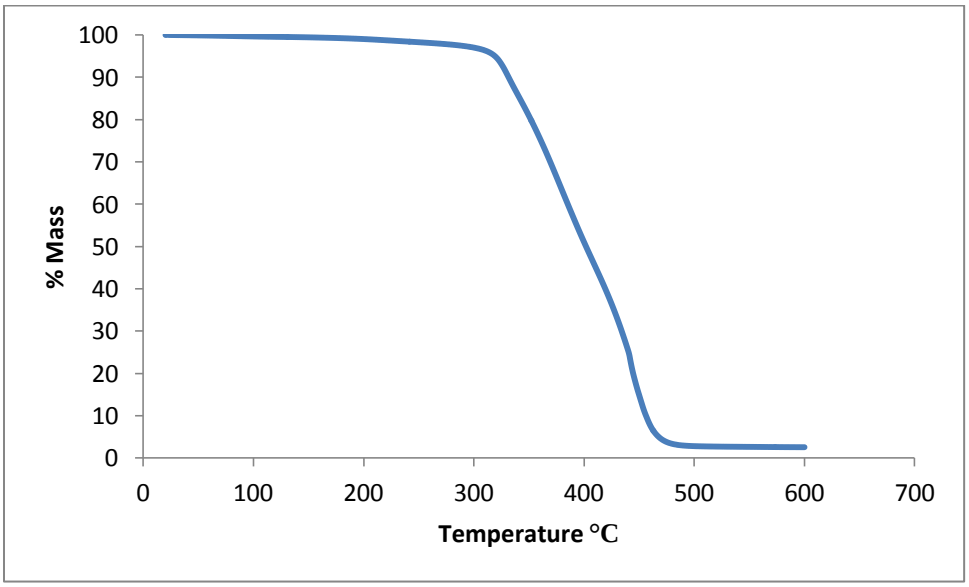


Figure 2.28: Thermal degradation of unknown polymer obtained in synthesis of RS(74/75)

2.6 Thermal Properties of the methacrylated mononers.

The thermal properties of the various monomers synthesised were investigated using TGA and DSC, giving rise to Tg, melting points (Tables 2.6 – 2.8) and thermal degradation information, (Figure 2.29).

Entry	Functionalisation	Monomer linker	Tg (°C)	M.P.
1	Unsaturated	CB**(60a)**	-36	80
2		CB**(60b)**	-45	88
3		CB**(60c)**	-	89
4		CB**(60d)**	-48	30
5		CB**(58/59)***	-37	31
6	Partially epoxidised (PE)	PECB**(71a)**	-48	81
7		PECB**(71b)**	-	79
8		PECB**(71c)**	-42	85
9	Fully epoxidised	CB**(71a)**	-42	85
10		CB**(71b)**	-45	81
11		CB**(71c)**	-38	85

'-': Denotes a monomer where Tg was not observed in the DSC curve.
*: Mixture of mono- and di- methacrylated monomers **(58)** and **(59)**.

Table 2.6: Glass transition temperatures and melting points of cocoa butter derived monomers

Entry	Functionalisation	Monomer linker	Tg (°C)	M.P.
1	Unsaturated	RS**(60a)**	-46	70
2		RS**(60b)**	-48	75
3		RS**(60c)**	-41	67
4		RS**(60d)**	-50	40
5		RS**(58/59)***	-51	15
6	Partially epoxidised (PE)	PERS**(71a)**	-38	70
7		PERS**(71b)**	-40	74
8		PERS**(71c)**	-40	70
9		PERS**(71d)**	-48	36
10	Fully epoxidised	RS**(71a)**	-41	70
11		RS**(71b)**	-38	78
12		RS**(71c)**	-	71
13		RS**(71d)**	-50	61

'-': Denotes a monomer where Tg was not observed in the DSC curve.
*: Mixture of mono- and di- methacrylated monomers **(58)** and **(59)**.

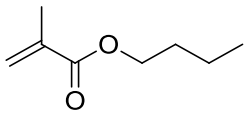
Table 2.7 Glass transition temperatures and melting points of rapeseed oil derived monomers

Entry	Functionalisation	Monomer linker	Tg (°C)	M.P.
1	Unsaturated	SB**(60a)**	-43	88.5
2		SB**(60b)**	-40	64
3		SB**(60c)**	-43	76
4		SB**(60d)**	-51	41
5		SB**(58/59)***	-50	15
6	Partially epoxidised (PE)	PESB**(71a)**	-38	74
7		PESB**(71b)**	-38	65
8		PESB**(71c)**	-40	79
9		PESB**(71d)**	-54	40
10	Fully epoxidised	SB**(71a)**	-39	70
11		SB**(71b)**	-42	66
12		SB**(71c)**	-46	79
13		SB**(71d)**	-47	50

'-': Denotes a monomer where Tg was not observed in the DSC curve.
*: Mixture of mono- and di- methacrylated monomers **(58)** and **(59)**.

Table 2.8: Glass transition temperatures and melting points of soybean oil derived monomers

Looking at Tables 2.6-2.8 all of the Tgs for the methacrylated monomers are between -37 - -54 °C, these low temperatures are characteristic of soft monomers.



(76)

Figure 2.29: Commercial soft monomer - nBMA

It is usually observed that the longer the carbon chain on the ester of a methacrylate acrylate functionality the lower the Tg.[155,156] With the shorter chained BMA **(76)** (Figure 2.29) having a Tg between 21 – 28 °C.[157] This is due to the longer chains making the back-bone more flexible. The ester linked methacrylate monomers **(60d)** and **(71d)** exhibit lower Tg's than the amide derivatives **(60a-c)** and **(71a-c).** A similar trend is observed for the melting points. A marked difference in melting point is observed between all the amide linked methacrylate monomers compared to the ester linked methacrylate counterparts (e.g. CB**(60a**) 80 °C > CB**(60d**) 30 °C, RS**(60a**) 70 °C > RS**(60d**) 40 °C, SB**(60a**) 88 °C > CB**(60d**) 41 °C). This is presumably due to the increased H-bonding observed for the amide derivatives. The melting points of the soybean (SB) and rapeseed (RS) derivatives are very similar this is presumably due to their similar structures. The cocoa butter (CB) monomers generally have higher melting points, this likely due to their more saturated structure. The lowest melting points are generally observed for the branched ester linked derivatives of Thames notably CB**(58/59**) 31 °C, RS**(58/59**) 15 °C CB**(58/59**) 15 °C. This makes sense as the branching will impede close packing of the molecules in the solid state. There seems to be no noticeable trend in comparing the melting points of the lengthening series of linkers (C-2, C-4, C-6) between the fatty acid chain and the methacrylate groups.

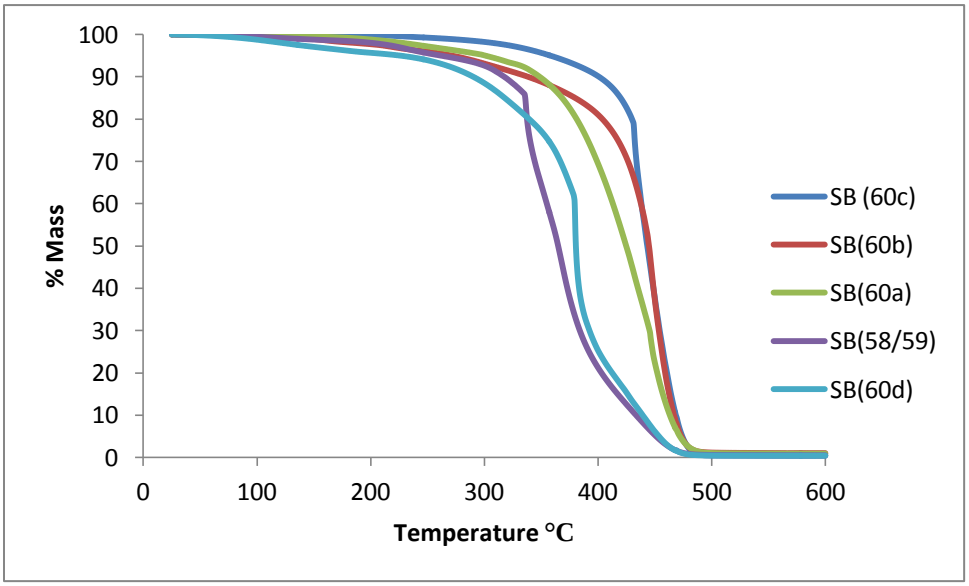


Figure 2.30: Thermal degradation of unsaturated soybean monomers with different amide linkers SB(60a-d) and SB(58/59)

Analysis of TGA shows that the ester linked methacrylate monomers derived from diethanolamine SB**(58/59)** and ethanolamine SB**(60d)** have less thermal stability and degrade at a lower temperature (approx. 50 ˚C lower) than the amide linked methacrylate monomers SB**(60a-c)**. Although this trend can be seen for the soybean monomers in Figure 2.30 it was also observed for all the cocoa butter and rapeseed derivatives as well. This makes sense as the amide linkages are inherently more stable than the corresponding ester linkages. Interestingly as the linking chain length increases in the series SB**(60a-c)** thermal stability increases and the degradation event appears to occur over a shorter temperature range. The ester derivatives SB**(58/59)** and SB(**60d)** appear to have multiple degradation events occurring over a larger temperature range.

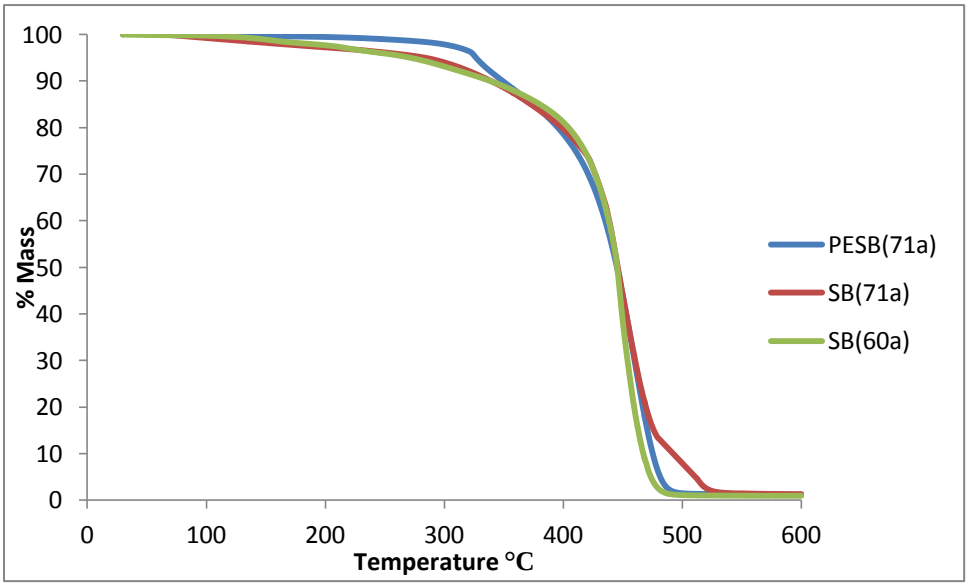


Figure 2.31: Thermal degradation comparing the effect of unsaturation, epoxidation and partial epoxidation on the monomer SB(60a)

TGA analysis of a series of soybean methacrylate monomers containing an ethylenediamine link indicate similar profiles for unsaturated SB**(60a)**, epoxidised SB**(71a)** and partially epoxidised PESB**(71a)** materials. The profile for the epoxidised derivative SB**(71a)** appears to show a higher temperature stability with the % mass loss occurring at 300 ˚C compared to just under 200 ˚C for the unsaturated monomer SB**(60a)**.

2.7 Direct Functionalisation of Triglyceride

A third approach for preparing monomers suitable for polymerisation, this time direct from triglycerides in one step was investigated. This involved adding a nucleophile (e.g. allyl amine, allyl alcohol, HEMA) already containing a

polymerisable group to the triglyceride. Synthesis of allyl derivatives would provide less reactive monomers than the methacrylate.

2.7.1 Addition of Allyl Amine and Allyl Alcohol

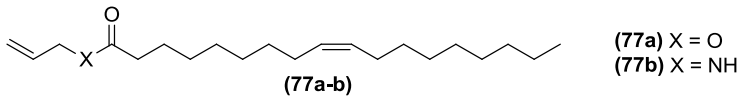


Figure 2.32: Direct addition of an allyl functionality

Both allylamine and allyl alcohol were successfully incorporated into the fatty acids to give monomers **(77a-b)**, (Figure 2.32). Hence, rapeseed oil was reacted with a slight excess of allylamine with NaOMe at RT over 6 hours without solvent to give the amide product **(77b**). The reaction gave a yellow oil; however it did not go to completion as the crude ^{1}H NMR showed some triglyceride remaining. On further purification by column chromatography a white solid was obtained in 56 % yield. The allyl ester derivative **(77a)** was prepared in the same manner but at 60 ˚C (due to the higher boiling point of allyl alcohol 95 ˚C compared to allyl amine 55 ˚C), to give the monomer as a clear oil in a higher 72 % yield. Both the monomers **(77a-b)** derived from this method were much easier to work with than the previous methacryloyl and styrene monomers. Due to the less reactive nature of the terminal allylic double bond they were much easier to handle without worry of premature polymerisation if not kept below room temperature.

2.7.2 Addition of 2-Hydroxyethyl Methacrylate

In the previous section (see 2.4.2) the methacrylate group was added to the amine or alcohol functional groups of fatty amides using methacryloyl chloride, primarily due to the ease of reaction and its availability. However in industry this is not a commonly used reagent, due in part to its toxicity. HEMA is a hydroxyalkyl ester monomer **(78)**, and was one of the first successful monomers used in the production of flexible contact lenses.[158] Due to its hydroxyl functionality, it might be utilised in a glycerolysis reaction to directly add methacrylate functionality to a vegetable oil, producing a one step synthesis of a fatty acid derived macromonomer (Figure 2.33). However, due to HEMA also containing an ester linkage, self transesterification of HEMA could also occur to give a dimethacrylate **(79)** (Figure 2.33).

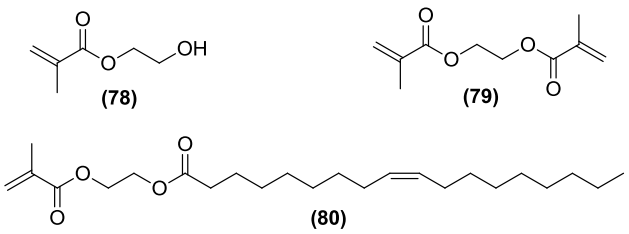


Figure 2.33: Monomers based upon 2-hydroxyethyl methacrylate (HEMA) (78).

Rapeseed oil was reacted at room temperature with 3 equivalents of HEMA and 3 equivalents of NaOMe at RT in a method very similar to the aminolysis discussed earlier in the chapter (see section 2.4.1). Unlike the previous monomers synthesised **(60a-d)**, this monomer **(80)** was a yellow oil, making it much easier to handle than the amide based materials **(60a-d)** and **(58/59)** which were either low melting point solids or very viscous liquids. The crude ^{1}H NMR showed the disappearance of the

glyceride peaks that are characteristic of triglycerides, the disappearance of the ethyl protons on the HEMA at 4.18 and 3.76 ppm, and the appearance of one peak at 4.32 ppm (corresponding to the CH_2O HEMA back-bone in the desired monomer **(80)**). In the crude spectra the appearance of singlets at 4.27 and 3.66 ppm indicated that there was self transesterification taking place between two molecules of HEMA under the reaction conditions to give a mixture of **(79)** and ethylene glycol **(81)**, (Figure 2.34).

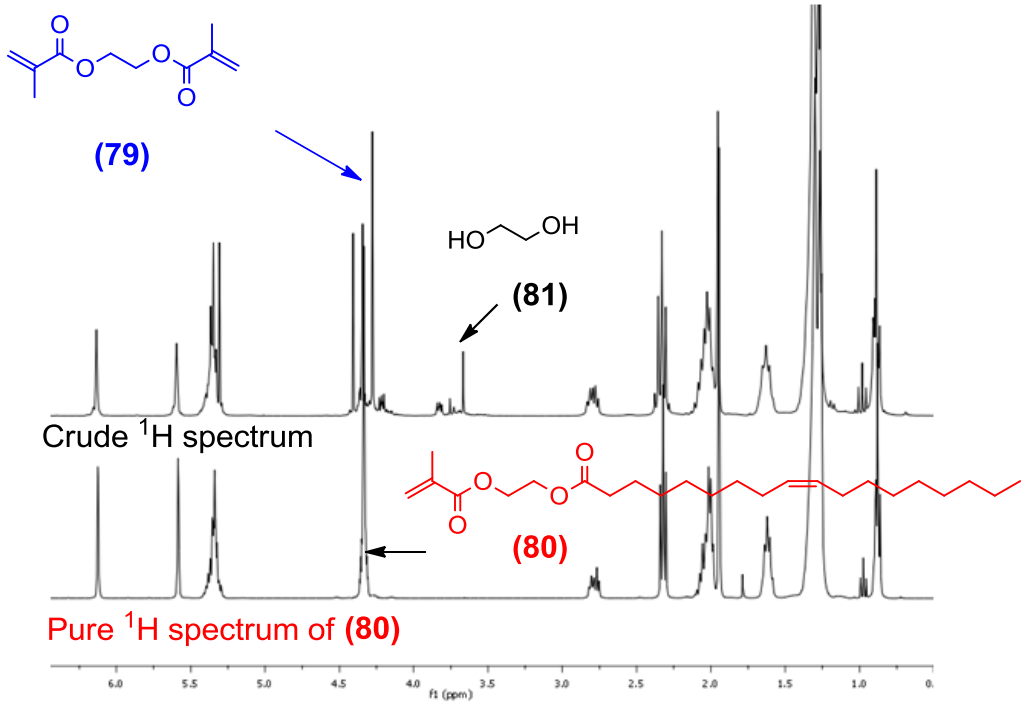


Figure 2.34: Crude and pure ^{1}H NMR of HEMA functionalised macromonomer RS(80)

2.8 Summary

A selection of monomers were synthesised using three different triglycerides (soybean oil, rapeseed oil and cocoa butter) by aminolysis with 5 different amine

linkers **(62a-e)**, both amino alcohol **(62d-e)** and diamine **(62a-c)** derived for the purpose of incorporation into polymer latexes (see Chapter 3). This gave 3 x 5 matrix of 15 monomers. The epoxidation of the unsaturation within the fatty chains of these 15 monomers was investigated as a way to remove the alkene functionality from the fatty chain but retain the 'kink' of the chain and determine the effect on incorporation into polymer latexes and the yellowing found in paint derived from these latexes.

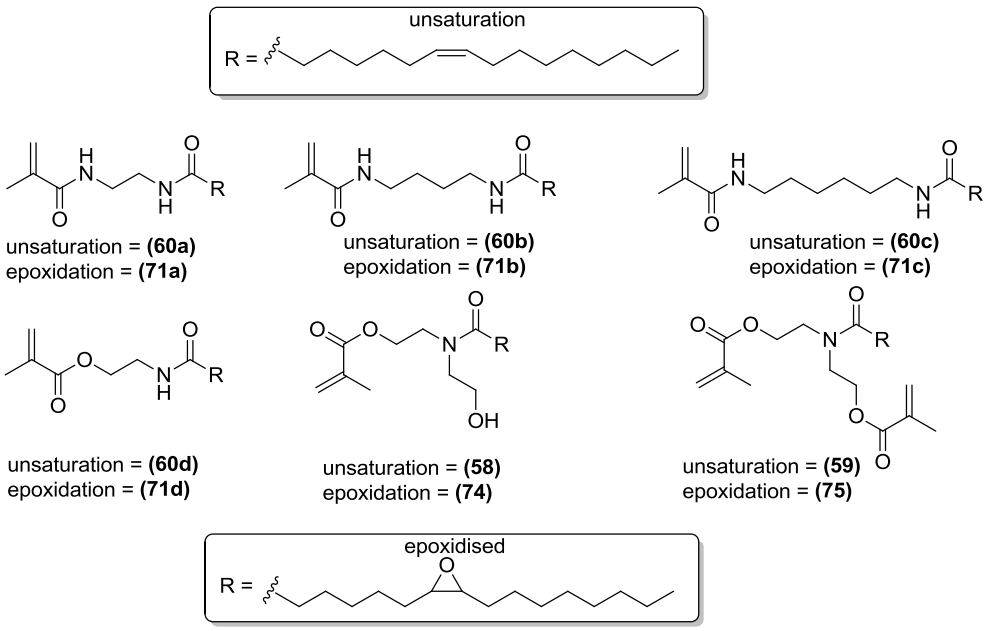


Figure 2.35: Functionalised fatty amide monomers with or without epoxide group

The synthesis of monomers with alternative polymerisable functionality (styrene RS**(68d)** and maleate RS**(70a/b)**) was also investigated *via* a two step approach, but others containing (HEMA RS**(80)**, allylamine RS**(77b)**, allyl alcohol RS**(77a)**) in a one step protocol. While it as possible to prepare the monomers **(60a-d)**, **(58/59)**, **(71a-d)**, and **(74/75)** on a large scale (> 100g), the other novel monomers **(68d)**,

(70a/b), **(80)**, and **(77a/b)** were only trialled on small scale (1-2 g) and so were not tested for viability in mini-emulsion polymerisation. The thermal properties, DSC and TGA of the majority of the new monomers was measured.

Chapter 3.0 Preparation of Polymer Latexes and Effect of Structure on Yellowing

This chapter will focus on the preparation of polymer latexes using a selection of the biomonomers synthesised in Chapter 2. We also describe how the structure of different biomonomers affected the yellowing process of the latexes over time.

3.1 Introduction to Miniemulsion Polymerisation

Emulsion polymerisation is a commonly used application in the paint and coatings industry and can be used both on a lab and industrial scale. Unlike suspension polymerisation, where the monomer is insoluble in the polymerisation medium, and the initiator is soluble in the monomer, emulsion polymerisation utilises an initiator which is soluble in the polymerisation medium and not in the monomer. Due to this, initial polymerisation takes place in the aqueous phase. Generally this process utilises water, a surfactant, a water-insoluble monomer, for example styrene, and finally a water-soluble initiator.[159,160] An emulsion is then formed by stirring vigorously, followed by heating to produce free radicals, allowing free-radical polymerisation to commence with the help of the initiator. A “latex” is formed which is made up of many polymer particles, each one containing a number of polymer chains. The term latex initially referred to the 'milky' sap of certain plants including rubber trees, the sap of which is a colloidal suspension of rubber particles stabilised by proteins. The term also came to describe polymer colloids, either as 'synthetic latexes' or 'latexes'. These particles are usually between 40 - 800 nm in diameter and are dispersed in the continuous aqueous phase. In order to keep the particles stable

and to stop them from coalescing a surfactant is added which keeps them continually dispersed. The surfactant lowers the surface energy between the continuous and dispersed phases.

We chose to investigate miniemulsion polymerisation, as opposed to standard emulsion polymerisation, to incorporate our renewable monomers into polymer latexes. The main differences between the two techniques concern particle nucleation and the transport of the monomer within the system.[161] With emulsion polymerisation the emulsion is made up of large monomer droplets, "monomer reservoirs" (>1 μm) and free or micellar surfactant.

Initiation takes place in the aqueous phase and polymerisation occurs, gradually the new polymer is surrounded by dissolved monomer and surfactant, or absorbed by already present monomer micelles.[162,163] As the polymerization continues the monomer migrates through the aqueous phase from the "monomer reservoirs" to the site of polymerisation. With miniemulsion however, the monomer is already dispersed into stabilized monomer droplets of between 50-500 nm by pre-emulsification. This is formed by applying high shear to the system, this can be achieved *via* ultrasound or a high pressure homogeniser. In a good miniemulsion latex the particle size before and after polymerisation should be very similar, unlike with emulsion polymerisation where the particles will grow over the course of the reaction. We chose to investigate miniemulsion polymerisation over standard emulsion due to the highly hydrophobic nature of the intended monomers. Given that these monomers would be derived from vegetable oils, their hydrophobicity would cause slow migration from the monomer reservoir through the aqueous phase to the micelles. With miniemulsion you overcome this problem by having the monomers already dispersed as small droplets, so migration is unnecessary, (Figure 3.1).[136]

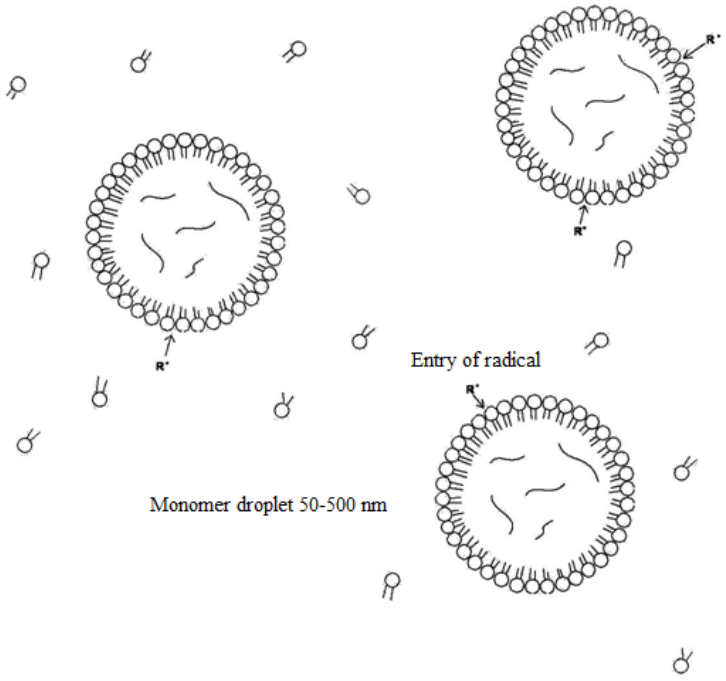


Figure 3.1: Schematic of miniemulsion

This approach of forming latexes is useful for our purposes because on drying, the latexes can form cohesive films. The film formation process starts with the latex particles suspended in water; this can be cast onto a flat surface. The polymer particles are able to move closer together as the water evaporates with the particles tending to pack in a hexagonal or a face-centred cubic fashion, (Figure 3.2). However in dispersions containing different particle sizes order is often not achieved, and high ionic strength can also cause disorder when packing, unless a high concentration of polymer is achieved. Gradually more water evaporates until a void free structure can be realised.

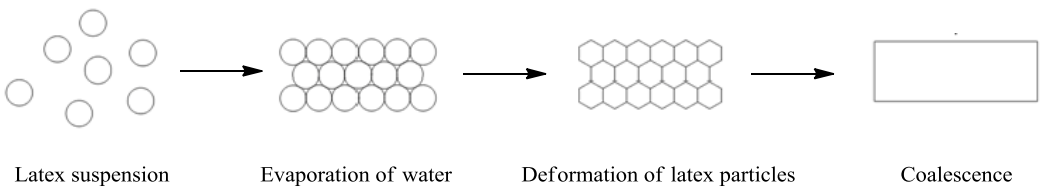


Figure 3.2 Film formation process

If the polymer has a low enough Tg the particles are then able to coalesce with interdifusion of the polymer chains allowing for a strong uniform film. Polymers with higher Tgs can be used with the aid of a coalescing agent, however these are generally solvents and thus are VOCs, which would be counterproductive in this instance.

Recent work by Thames and co-workers, has looked into the incorporation of vegetable oil based monomers (VOMMs) into waterborne systems *via* miniemulsion polymerisation.[136] They were looking for ways to successfully incorporate the advantages of oil-modified polyesters with waterborne systems, and to reduce the VOCs in these waterborne coatings. Using conventional emulsion polymerisation would be challenging due to the highly hydrophobic nature of the VOMMs, meaning diffusion through the aqueous phase would be slow. Instead miniemulsion was studied, initially with triglyceride derivatives **(82)** and **(83)** derived from soybean, (Figure 3.3).

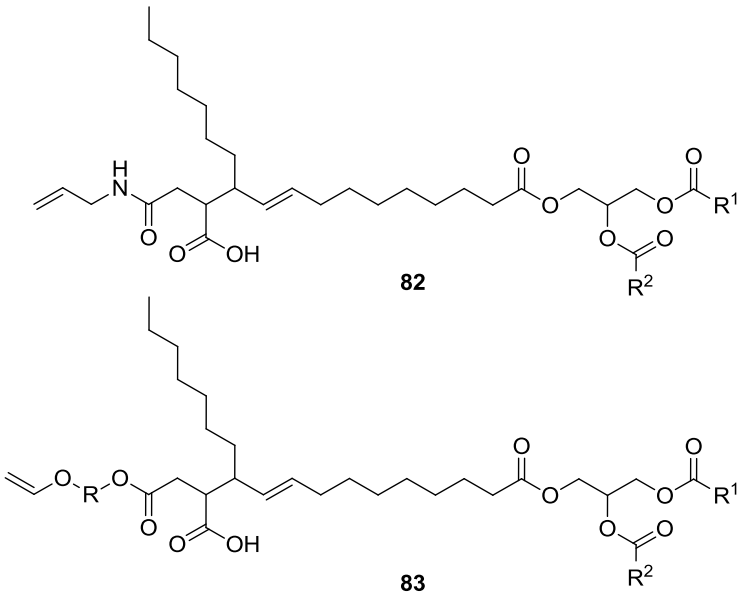


Figure 3.3 Idealised structures of 2 soybean oil based macromonomer used in miniemulsion studies[164]

Their studies concluded that the VOMM **(82)** and **(83)** could be successfully incorporated into the polymer backbone of latexes at 35 wt%. It was postulated that unsaturation in the VOMM backbone was preserved during polymerisation and that these intact double bonds could potentially undergo oxidative cross-linking during the curing process.

During the course of our studies Thames *et al.* published the use of glycerol free amide functionalised vegetable oil derivatives **(58/59)** and **(60d)** in latexes.[137] These monomers are closely related in structure to ours **(60a-c)** described in chapter 2. These monomers were derived from the reaction of vegetable oils such as soybean oil with ethanolamine **(62d)**, substituted ethanolamines **(62e)** and diamines **(60a-c)**, followed by the addition of methacrylic acid or methacryloyl chloride to give polymerisable functionality, (Figure 3.4). *Consequently, in this chapter we investigate the use of related solid diamide derivatives **(60a-c)** in latex formation and compare them to those liquid biomonomers described by Thames **(58/59**)* and **(60d)**. It would be difficult to compare the results from our biomonomers **(60a-c)** with the Thames group monomers **(58/59)** and **(60d)** directly as they only described one latex example with little data given on its properties. Hence we chose to prepare the Thames monomers **(58/59)** and **(60d)** and prepare latexes from them ourselves.

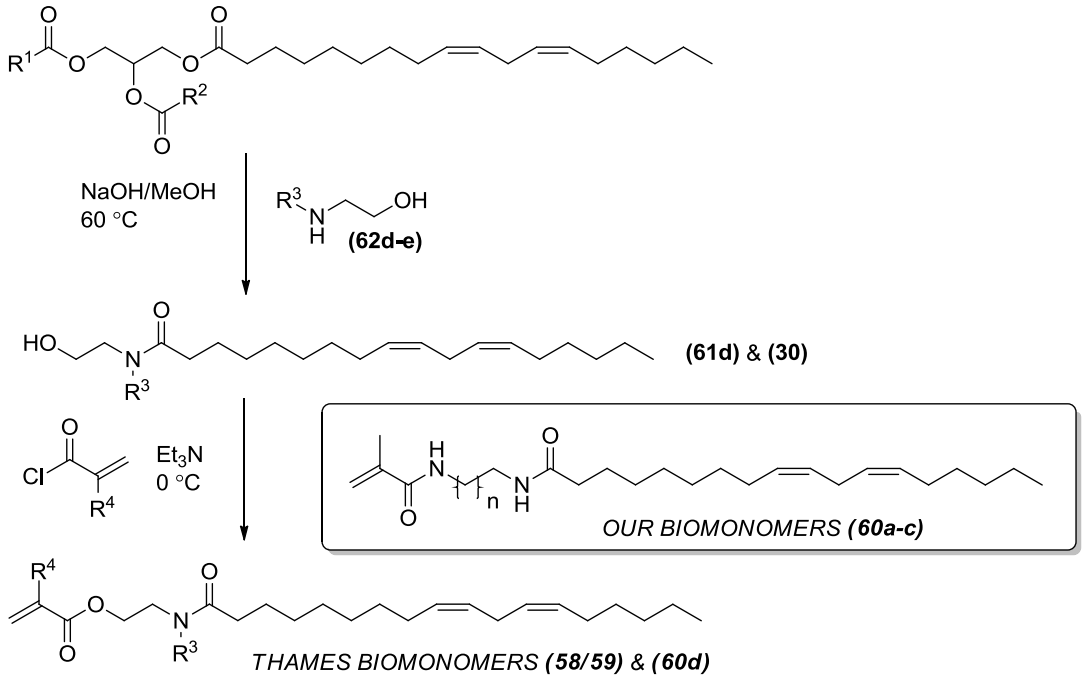


Figure 3.4: Idealised structure of glycerol ester free VOMMs

They also described a second approach using urethane linked molecules **(85**), (Figure 3.6). In this approach hydroxyethylmethacrylate (HEMA) was initially reacted with isophorone diisocyanate in hexane, with phenothiazine, methyl hydroquinone and dibutyl tin dilaurate (DBTDL) as additives, to give urethane **(84)**, (Figure, 3.5).

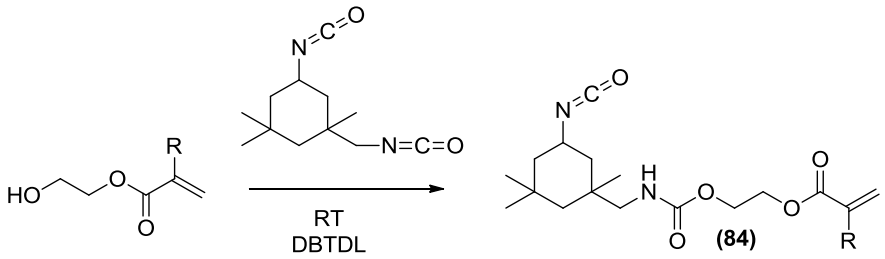


Figure 3.5: Reaction of isophorone diisocyanate with HEMA

The macromonomers **(85)** were finally synthesised by reacting the hydroxyl functional fatty amide **(60d)** with the novel isocyanate **(84)** to afford a urethane fatty amide **(85)**, (Figure 3.6).

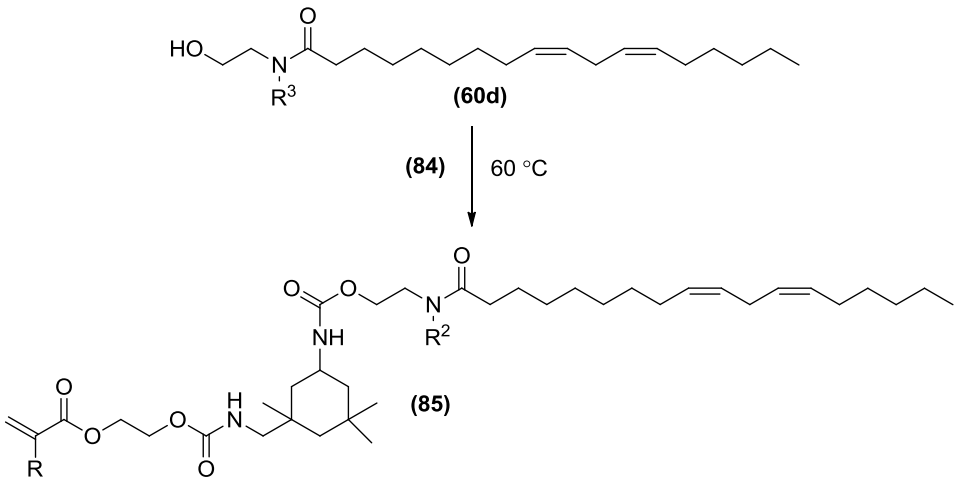


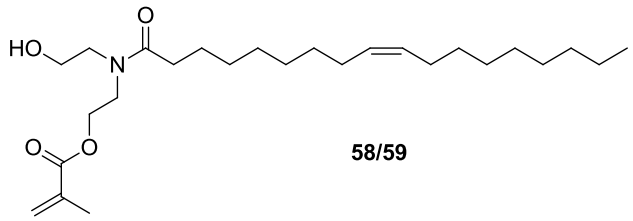
Figure 3.6: Synthesis of urethane fatty amide monomer

Both of these types of VOMMs **(58/59)**, **(60d)** and **(85)** were then incorporated into polymer latexes *via* miniemulsion polymerisation.

3.2 Latex Preparation

3.2.1 Initial Large Scale Trials of Latex Formation Using Biomonomer (58/59)

Initial trial polymerisations were carried out on a 1 kg scale (using 38.1 g of known Thames biomonomer **(58/59)**, to check conditions) in the Akzo Nobel laboratories with butyl methacrylate monomer (BMA). The polymerisation was undertaken in a flat-bottomed vessel submerged in a water bath with a propeller stirrer, nitrogen inlet and condenser.



58/59

Figure 3.7: Large scale reactions using monomers (58/59)

	Solids (g)	Volatiles (g)	Weight (g)	% of latex
Monomer emulsion				
Water	-	371.7	486.1	48.6
Disponil® 1580	38.1	-	38.1	3.81
BMA	341.1	-	341.1	34.1
Biomonomer	38.1	-	38.1	3.81
Hexadecane	30.5	-	30.5	3.05
Methacrylic acid	1.91	-	1.91	0.19
Oxidant initiator				
t-Butyl perbenzoate	3.81	-	3.81	0.38
Reductant initiator				
Water	-	45.7	45.7	4.54
Ascorbic acid	1.72	-	1.72	0.17

Table 3.1: Table showing 'recipe' for large scale miniemulsion polymerisation of biomonomers and BMA

	Solids (g)	Volatiles (g)	Weight (g)	% of Latex
Oxidant				
t-Butyl hydroperoxide	1.33	0.57	1.91	0.19
Reductant				
Water	-	7.62	7.62	0.76
Sodium metabisulphite	3.35	-	3.35	0.33

Table 3.2: Table showing the large scale miniemulsion 'mop-ups' used to insure polymerisation is terminated.

The monomer emulsion was prepared using materials listed in Table 3.1 in an ice bath using a Branson rotor-stator homogeniser for 20 minutes at 400 rpm. Once emulsified, 10 % of this monomer emulsion and 10 % of the reductant portion of the initiator (Table 3.1) were placed in the flask and heated to 60 °C under a blanket of

nitrogen. The remaining monomer emulsion and reductant portion of the initiator was added simultaneously *via* peristaltic pumps over 3 hours, under a nitrogen atmosphere at 60 °C in a seed feed method. After addition was complete further reductant and oxidant (Table 3.2) were added and the temperature held at 60 °C to insure a complete polymerisation. The latex was cooled and filtered subsequent to film and latex testing (see Section 3.3-3.6). A semi-continuous style method, although unusual, was implemented as ideally the method would be scaled up in industrial practice, where a batch method would be inadvisable.

3.2.2 Initial Reactions in University Laboratory

On transfer of this process to the university laboratories a number of aspects of this method were modified so that latexes were prepared on a 175 g scale instead of 1Kg. This was to allow for polymerisation to take place in a 250 mL reactor vessel fitted with a water jacket for efficient heating as well as the difficulty in preparing large quantities of all the biomonomers needed for testing, (Figure 3.9). Due to the smaller scale and the unavailability of peristaltic pumps the seed feed process was not initially used. Instead a batch style process was implemented; all of the monomer emulsion was placed into the reaction vessel after emulsification, and heated to 60 °C under nitrogen. The initiator was added in 6 x 1.33 mL batches using a syringe over 3 hours. The surfactant was changed from the industrially used non-ionic disponil® to the anionic sodium dodecyl sulphate (SDS). The change was made due to limited availability of disponil and that anionic surfactants (such as SDS) have wide-spread application in emulsion polymerisation.[165]

Two monomers were trialled using this method, our novel monomer RS**60a** and the analogous ester monomer RS**(60d)** reported by Thames *et al*. These monomers were derived from rapeseed oil (RS) and their synthesis was described in Chapter 2.

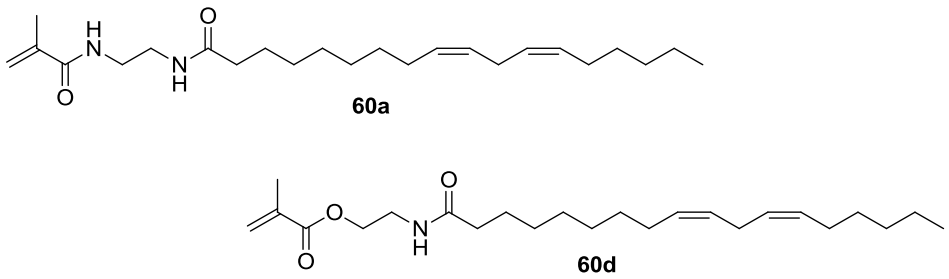


Figure 3.8: Monomers tested in polymerisation

The work of Thames suggested that because **(60d)** was known to incorporate well into polymer latexes then **(60a)** should as well.[137] However, the diamide monomers were low melting point solids, as opposed to the liquids used by Thames, and it was not certain how this and the fact that the diamide monomers would exhibit greater H-bonding, would affect latex formation and film properties. However, it was found that on addition of the initiator and on commencement of heating, gelation occurred with both monomers; this was not seen in the industrial laboratory. This gelation indicates that the emulsion particles lacked stabilisation. With the 'reactor' in miniemulsion being the monomer containing micelles created on emulsification it is important to establish very stable micelle particles. A number of factors could be the cause of the observed instability in the reactions of **(60a**) and **(60d**) including the particle size and surfactant used. The surfactant is extremely important as both the type and amount can affect the droplet size. As stated previously, in the polymerisations implemented in the university laboratories, all of the monomer emulsion was added to the reaction vessel at the beginning of the polymerisation.

Although unlikely as batch polymerisation is used widely, this could have had an effect on the polymerisation.

Consequently we modified the process so that the monomer was added slowly over the course of 3 hours (as in the original industrial scale method), effectively giving more control over the polymerisation. The surfactant was also switched to disponil® in place of SDS to mimic as closely as possible the successful conditions implemented for the large scale trials.

3.2.3 Polymer Latex Preparation Used

After a number of initial experiments an optimised protocol was achieved for incorporating both the ester derived RS**(60d)** and amide derived RS**(60a)** biomonomers into polymer latexes. This included firstly preparing the monomer emulsion by blending water (continuous phase), surfactant, monomers (dispersed phase), hydrophobe (osmotic pressure agent) and the oxidant portion of the initiator together *via* a Branson sonifier for 10 minutes in an ice bath to give a stabilized monomer emulsion, with an average particle size of <300 nm, (Table 3.3). Secondly, ~10% of the resulting monomer emulsion and ~ 10% of the reductant portion of the initiator (Table 3.3) were placed into a flat bottomed reactor vessel (Figure 3.9) under a 'blanket' of nitrogen and heated to 60 °C using a water pump, and jacket. All latexes were prepared using the same 'recipe' as shown in Tables 3.3 and 3.4.

	Solids (g)	Volatiles (g)	Weight (g)	% of latex
Monomer emulsion				
Water	-	78.5	78.5	44.9%
Disponil® 1580	7.28	-	7.28	4.16
BMA	59.2	-	59.2	33.8
Biomonomer	6.62	-	6.62	3.78
Hexadecane	5.29	-	5.29	3.02
Methacrylic acid	0.33	-	0.33	0.19
Oxidant initiator				
t-Butyl perbenzoate	0.66	-	0.66	0.38
Reductant initiator				
Water	-	7.94	7.94	4.54
Ascorbic acid	0.30	-	0.30	0.17

Table 3.3: Table showing 'recipe' for miniemulsion polymerisation of biomonomers and BMA

The vessel was fitted with an overhead stirrer, with propeller stirrer, pressure equalised dropping funnel and water cooled condenser. The remaining monomer emulsion was added over 3 hours *via* a dropping funnel, whilst stirring at 60 °C under a nitrogen atmosphere. The remaining reductant portion of the initiator was added in 6x1.33 mL batches every 30 minutes *via* syringe.

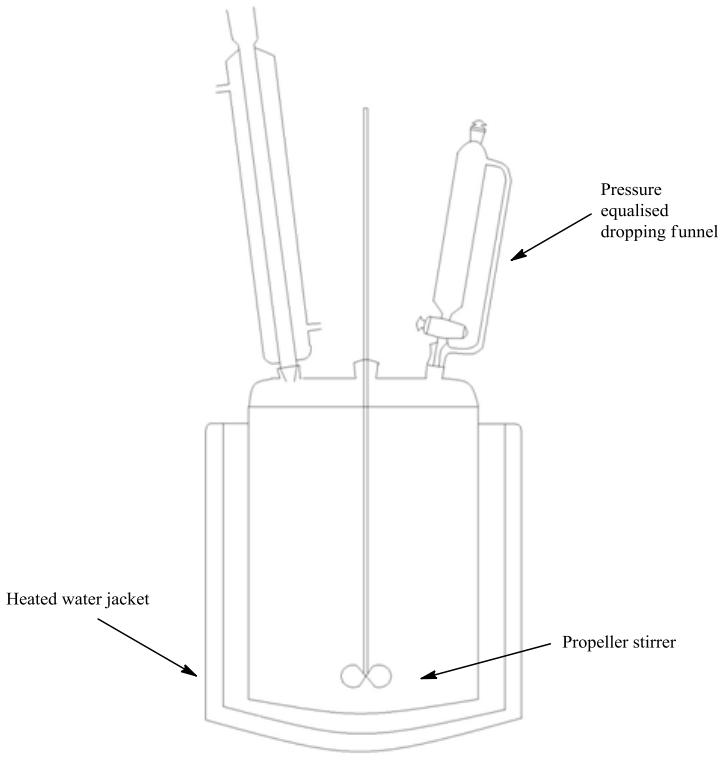


Figure 3.9: Reaction vessel set up for miniemulsion polymerisation.

Due to a slight exotherm in the reaction, the temperature was monitored to ensure a constant temperature. Disponil® 1580 was used as a non-ionic surfactant. This class of surfactants are usually fatty alcohols or ethers derivatives of fatty alcohols.[166]

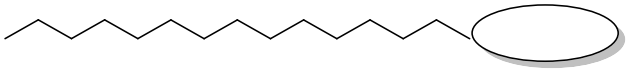


Figure 3.10: Non-ionic Surfactant, where the head (hydrophilic end) is neither cationic nor anionic.

Due to the use of a non-ionic surfactant, deionised water was not used at all during the process. A small amount of hexadecane was used as a 'super hydrophobe'.[167] These are usually used in a miniemulsion systems to avoid Ostwald ripening. This is a destabilisation process that can occur, due to the energy favourability of forming larger particles or crystals compared to that of the higher energy smaller particles.[168] With this process you are not seeing coalescence like with coagulation, but instead you have the migration of the smaller droplets through the aqueous phase and into the larger droplets.

After complete addition of the initiator and monomer emulsion a further oxidant and reductant is added to insure polymerisation had finished (Table 3.4).

	Solids (g)	**Volatiles (g)**	**Weight (g)**	**% of Latex**
Oxidant				
t-Butyl hydroperoxide	0.23	0.10	0.33	0.19
Reductant				
Water	-	7.94	7.94	4.54
Sodium metabisulphite	0.58	-	0.58	0.33

Table 3.4: Table showing the miniemulsion 'mop-ups' used to insure polymerisation is finished

The latex was then cooled and filtered ready for analysis. Assuming complete polymerisation of BMA and incorporation of biomonomer the percentage of solids within the latex should be ~38%, with a total percentage of solids, including all non-volatile aspects of the latex measurable at ~46% of the total latex. In order to determine the conversion of polymerisation and whether the biomonomer had been incorporated into the product a range of tests were performed. *BMA conversion*: after polymerisation was complete the conversion of the BMA could be measured by gravimetry, as the monomer is volatile. A small amount of latex was dried at high heat to remove all of the volatiles to leave just the solids. *Biomonomer conversion*: the biomonomer, however, is not volatile and so the conversion had to be measured by extraction of the dry film with hexane. The weight loss can then be measured to see how much of the biomonomers had remained. These together gave the total conversion for both monomers.

3.2.4 Latex Formation: Comparison of Different Biomonomers.

Having established a procedure for the preparation of the latexes, we then examined the latex forming ability of the complete range of 15 unsaturated **(58/59)**, **(60a-d)**, 11 partially epoxidised (PE) **(74/75)** and PE**(71a-d)** and 11 fully epoxidised biomonomers **(74/75)** and **(71a-d)** derived from the three oils, rapeseed (RS), soybean (SB) and cocoa butter (CB) described in Chapter 2.

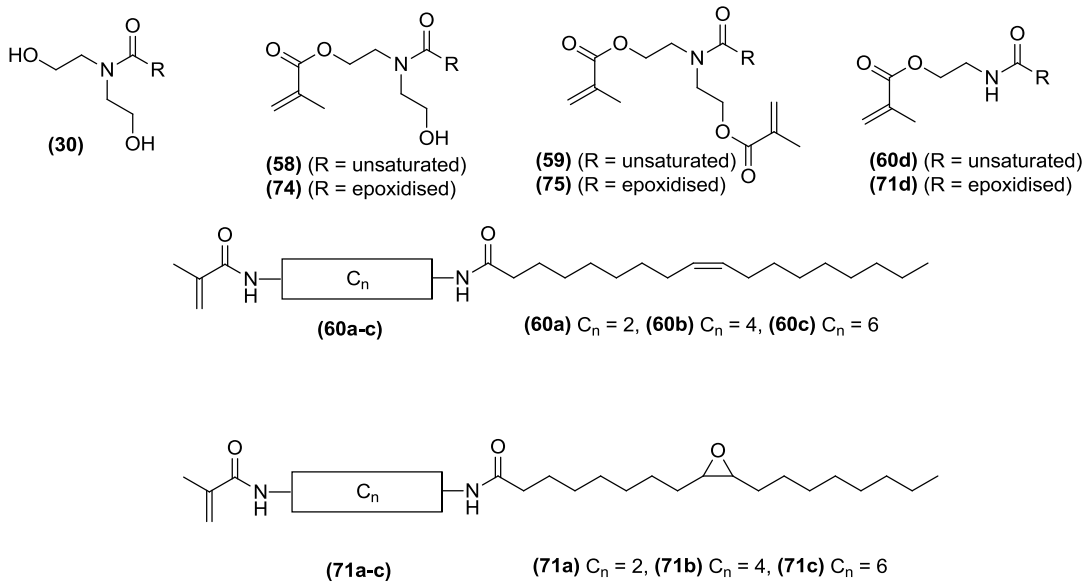


Figure 3.11: Summary of unsaturated, partially epoxidised and fully epoxidised monomers derived from soybean oil, rapeseed oil and cocoa butter

The process outlined in Section 3.2.3 was used to polymerise all 37 of the monomers. Difficulties were found when attempting to incorporate all the cocoa butter based monomers into both the monomer emulsions and subsequently their polymer latexes. Monomers derived from cocoa butter are more saturated (with higher mp's) than those of the other oils. As well as finding it more difficult to dissolve these monomers sufficiently it was also found that as the monomer emulsion cooled down after sonication and subsequent to addition into the reactor vessel, gelation was often observed. In an attempt to avoid gelation, all of the CB monomer emulsion was added into the reactor vessel at the start of the polymerisation, allowing all of the emulsion to be kept at 60 °C, and thus liquid. The initiator was then, as with the previous method added over the course of three hours, followed by the 'mop ups' (Table 3.4). Difficulty was also seen when trying to incorporate the fully epoxidised monomers of all the three vegetable oil based systems into the latexes. The more epoxides present in the biomonomer (e.g

SB**(60a-d)**) the more difficult incorporation was to achieve. Presumably, for the same reason as above (higher mp's or worse solubility). Table 3.5 indicates which monomers were successfully incorporated into latexes (Y) and underwent further study and those that were eliminated at this stage (N). Consequently, only a small number of cocoa butter derived monomers (CB**(60a-c**), CB**(58/59)**) and fully epoxidised monomers (**RS(60b-d)**) were used further in this study.

Linker	Rapeseed (RS)			Cocoa butter (CB)			Soybean (SB)		
	Unsat.	Partial	Full	Unsat.	Partial	Full	Unsat.	Partial	Full
(60a/71a)	Y	Y	N	Y	N	N	Y	Y	N
(60b/71b)	Y	Y	Y	Y	N	N	Y	Y	N
(60c/71c)	Y	Y	Y	Y	N	N	Y	Y	N
(60d/71d)	Y	Y	Y	N	-	-	Y	Y	N
(58/59/74/75)	Y	Y	-	Y	-	-	Y	Y	-

Unsat. = unsaturated, Partital = approx. 50 % of double bonds removed *via* epoxidation, Full = all double bonds removed *via* epoxidiation
Y = Successful incorporation into latex, N = Failure to incorporate into latex

Table 3.5: Summary of failure or success of monomer incorporation into latexes

3.3 Properties of Latexes

Once polymerisation was complete for the 27 chosen biomonomers, (See Table 3.5) a number of different tests were undertaken to determine the properties of the latexes and their films; to see how useful they would be for use in various coatings.

3.3.1 Percentage Conversion, Particle Size and PDI

Firstly, the percentage conversion for both monomers (BMA and VOMM) was calculated. This was done *via* gravimetry and soxlet extraction as described earlier. The particle size along with the particles PDI was also measured using light scattering. A good particle size for miniemulsion would be in the region of 40 - 800 nm, with a PDI of 0 - 0.05, which is standard for a monodisperse sample.

Linker	Triglyceride	% Conversion			Particle Size (nm)	PDI
		BM	BMA	Total		
58/59	Cocoa Butter	86	91	90.5	132	0.07
	Rapeseed Oil	90	92	91.8	140	0.07
	Soybean Oil	90	93	92.7	153	0.08
60d	Rapeseed Oil	82	88	87.4	162	0.05
	Soybean Oil	89	95	94.4	167	0.05
60a	Cocoa Butter	81	85	84.6	177	0.08
	Rapeseed Oil	90	95	94.5	177	0.04
	Soybean Oil	91	94	93.7	181	0.05
60b	Cocoa Butter	84	87	86.7	187	0.05
	Rapeseed Oil	89	93	92.6	191	0.06
	Soybean Oil	89	93	92.6	152	0.03
60c	Cocoa Butter	83	86	85.7	186	0.06
	Rapeseed Oil	90	90	90	170	0.08
	Soybean Oil	84	89	88.5	174	0.05

BM = biomonomer, BMA = butyl methacrylate

Table 3.6: Unsaturated polymer latexes, % solids, conversion and particle size

With respect to the % conversions and the % of solids obtained it seems that the source of the oil seems to be more critical than the type of linking chain. In each case the cocoa butter latex conversions were lower compared with the other oils. This is likely due to issues found with the stability of the systems as mentioned before. More coagulum was also obtained with the cocoa butter latexes which could also account for the loss in solids and conversion. Coagulum is formed due to the colloidal instability of latex particles. It makes sense that the level of unsaturation (and hence 'kinks') in the chains will affect the properties of latexes and their formation. However, there seems to be little difference in the effect of the level of unsaturation on latex conversion between rapeseed and soybean derivatives and all of the latexes appear to show a good particle size in the right region with a similar polydispersity.

We next investigated the effect of partially epoxidising and fully epoxidising the alkene groups in biomonomer side-chain, see Tables 3.7-3.8. As stated above, the cocoa butter monomers were not satisfactory and so only rapeseed and soybean oil derivatives were assessed.

Linker	Triglyceride	% Conversion			Particle Size (nm)	PDI
		BM	BMA	Total		
74/75	Rapeseed Oil	90	90	90	185	0.07
	Soybean Oil	90	92	91.8	175	0.06
71a	Rapeseed Oil	91	95	94.6	164	0.09
	Soybean Oil	89	93	92.6	159	0.06
71b	Rapeseed Oil	88	90	89.8	159	0.05
	Soybean Oil	92	96	95.6	156	0.03
71c	Rapeseed Oil	90	93	92.7	180	0.07
	Soybean Oil	91	95	94.6	165	0.01

BM = biomonomer, BMA = butyl methacrylate

Table 3.7: Partially epoxidised polymer latexes % solids, conversion and particle size

Linker	Triglyceride	% Conversion			Particle Size (nm)	PDI
		BM	BMA	Total		
71a	Rapeseed Oil	92	95	94.7	169	0.09
71b	Rapeseed Oil	89	90	89.9	160	0.08
71c	Rapeseed Oil	89	92	91.7	182	0.10

BM = biomonomer, BMA = butyl methacrylate

Table 3.8: Fully epoxidised polymer latexes % solids, conversion and particle size

Again, analysis indicated very little difference between the different monomers studied. The highest conversions in most cases were obtained with soybean or rapeseed oil with the small tethered chain based upon ethylenediamine **(60a)**, PE**(71a)** and **(71a)** but the margins were small and an exception was SB**(71b)**.

Increasing the tether to a C-4 and C-6 link generally lowered the conversions marginally.

3.3.2 Film Casting and Hardness

A number of physical tests were carried out on the dry latex films. Firstly, all films were cast on to glass plates using a bar applicator to give a 75 nm thick film which was left to air dry. The clarity of the film was visually checked. Ideally the films should be clear and cohesive, with little to no shrinkage. The film should be smooth with no 'bits', or cracking/crazing. The hardness of the polymer films were measured using a Sheen pendulum hardness rocker. This method works by allowing a pendulum attached to a ball bearing to rest on the surface of a dry film, the number of swings of the pendulum can be counted and these are converted into seconds based on the calibration for the particular apparatus (1 oscillation = 1.2 s). It is based on the principle that the amplitude of the pendulums oscillation decreases quicker when supported on a softer film.

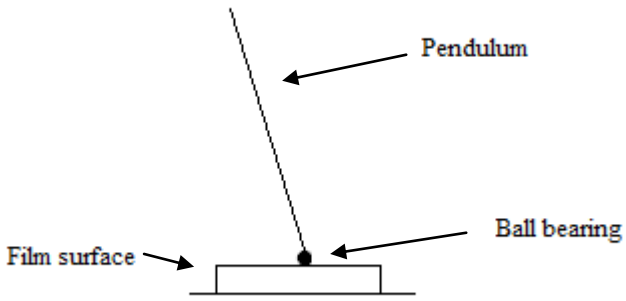


Figure 3.12: A simple schematic showing the Erichsen hardness test.

Linker	Triglyceride	Hardness (s)	Film
58/59	Cocoa Butter	20	Clear film
	Rapeseed Oil	23	Clear film
	Soybean Oil	23	Slight Bloom, cohesive
60d	Rapeseed Oil	24	Clear films, slight mottling and bloom over time
	Soybean Oil	32	Cohesive, slight bloom
60a	Cocoa Butter	23	Clear films, slight mottling and bloom over time
	Rapeseed Oil	23	Clear films, slight mottling and bloom over time
	Soybean Oil	29	A few bits, slight blooming
60b	Cocoa Butter	18	Clear. Some visible (air?) rings
	Rapeseed Oil	22	Clear films, slight mottling and bloom over time
	Soybean Oil	27	Slightly brittle, bloom
60c	Cocoa Butter	23	Very slightly hazy. Film appears thicker in centre.
	Rapeseed Oil	31	Some bits, brittle

	Soybean Oil	27	Clear, slight cracking (on limit of cohesion), brittle

Table 3.9: Unsaturated polymer latexes, hardness and film quality

Linker	Triglyceride	Hardness (s)	Film
74/75	Rapeseed Oil	29	Slight bloom, tough
	Soybean Oil	29	Some bits, on limit of coalescence, slight bloom
71a	Rapeseed Oil	25	Clear films, slight mottling and bloom over time
	Soybean Oil	23	Shrank, tough, slight bloom
71b	Rapeseed Oil	22	Hazy, not brittle
	Soybean Oil	31	Very bitty
71c	Rapeseed Oil	28	Clear films, slight mottling and bloom over time
	Soybean Oil	26	Clear good film

Table 3.10: Partially epoxidised polymer latexes hardness and film quality

Linker	Triglyceride	Hardness (s)	Film
71a	Rapeseed Oil	7	
71b	Rapeseed Oil	22	Clear films, slight mottling and bloom over time
71c	Rapeseed Oil	22	Clear films, slight mottling and bloom over time

Table 3.11: Fully epoxidised polymer latexes hardness and film quality

From study of the clarity of the films it can be seen that the latexes incorporating unsaturated monomers derived from longer amines (i.e. **(60b)** and **(60c)**) while they give clear films, also seem to give more brittle and harder ones. However, when the same amines are used in the partially or fully epoxidised films the films become less brittle and softer. Softer films are also observed for the more saturated derivatives based upon cocoa butter. Epoxidised oils are often used as plasticisers[169,170] and so could be acting in this role causing the decrease in brittleness observed within the films. For unsaturated films those derived from soybean tended to be harder with the exception of monomers based upon **(60c)**. Blooming was also observed; this occurs when 'oily' particles or residue gradually rise to the surface of a film. This could be due to incomplete incorporation of the biomonomer, differential polymerisation to form either homoBMA or homo-biomonomer blocks or due to residual unfunctionalised di-or triglyceride present in the biomonomer. An AFM image was

taken of a film using the unsaturated rapeseed oil and ethylenediamine derived monomer, RS**(60a)**, (Figure 3.13).

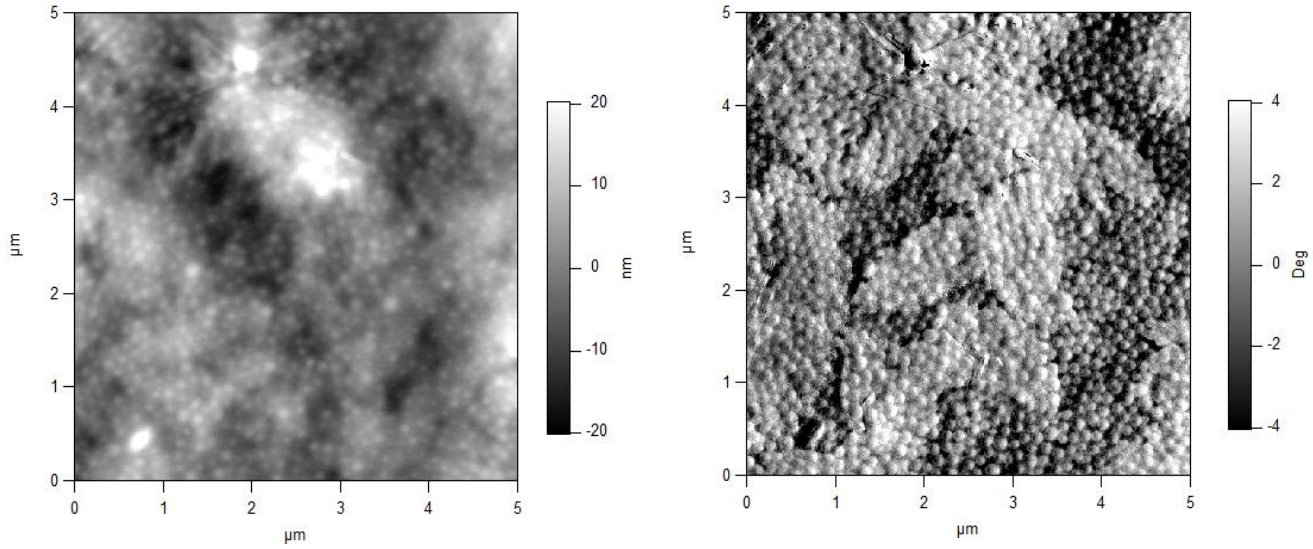


Figure 3.13: AFM images of polymer latex film a) height/topography b) Phase and potential change in material type.

Looking at the AFM images it seems likely that there are at least 2 types of phase, which in this case may be due to different levels of biomonomer incorporation or the existence of both homoBMA and homobiomonomer particles.

3.4 Molecular Weight

Gel permeation chromatography (GPC) was undertaken to obtain average molecular weights (Mw/Mn) of the polymer latexes prepared (see appendix B). Care must be taken in concluding too much from the data as the novel polymers were measured using methyl methacrylate standards. In most cases *N*-methyl pyrollidine (NMP)

seemed to be the best solvent for dissolving the latexes, however a large amount of gel material still had to be filtered out meaning the results given are not an accurate representation of the molecular weights and may be underestimating them. The molecular weight for a typical acrylic polymer are often in the 80.0 to 125.0 KDa however with the vegetable oil BMA copolymers we have seen lower weights. This could be due to the high gel content of these polymers as discussed or the VOMM's acting as chain transfer agents (Table 3.17). There is a general trend with the increasing amount of unsaturation in the oil to see a decrease in Mn, which could be attributed to backbiting within the chain during polymerisation. In general rapeseed derived latexes have a smaller Mn and PDI. Unsaturation in vegetable oils slows down polymerisation as they are much lower in reactivity than acrylates or methacrylates.

3.5 Minimum Film Formation Temperature (MFFT) and Tg.

Minimum film formation temperature is the temperature needed for a polymer latex to form a clear and cohesive dry film. It is important to measure this, as these latexes have a potential use in paint, and this temperature has a bearing on its application. A good MFFT is usually ~10 degrees lower than the temperature at which the paint or coating would be used. For example a good MFFT for an indoor decorative paint would be around 7-10 °C, ~ 10 degrees lower than room temperature. All of the latexes prepared in this chapter were measured using a 'Rhopoint MFFT bar 60'. This allows you to draw down a thin film of polymer latex on a nickel plated copper platen, using a cube applicator; this gives an even film thickness of 1 inch wide, 75 μm thick. The platen is heated and cooled to create a temperature gradient; in this case a range of 0 to 18 °C was used. After drying, you are able to visually see where

cohesive film forming takes place (MFFT). Below this temperature you will find the film is opaque white in colour and is often powdery, cracked, or cracks easily on touch whereas with temperatures above the MFFT you observe as clear continuous film.. To measure, the latex is dragged from the warm end to the cold end. The cover is then closed and left for ~ 2 hours to equilibrate before visual assessment.

Sensor	1	2	3	4	5	6	7	8	9	10
Approx temp.	0	2	4	6	8	10	12	14	16	18
Actual temp.	0.2	2.4	4.5	6.0	8.2	10.6	12.2	14.6	16.7	18.3

Table 3.12: Temperature range used on Rhopoint MFFT bar 60

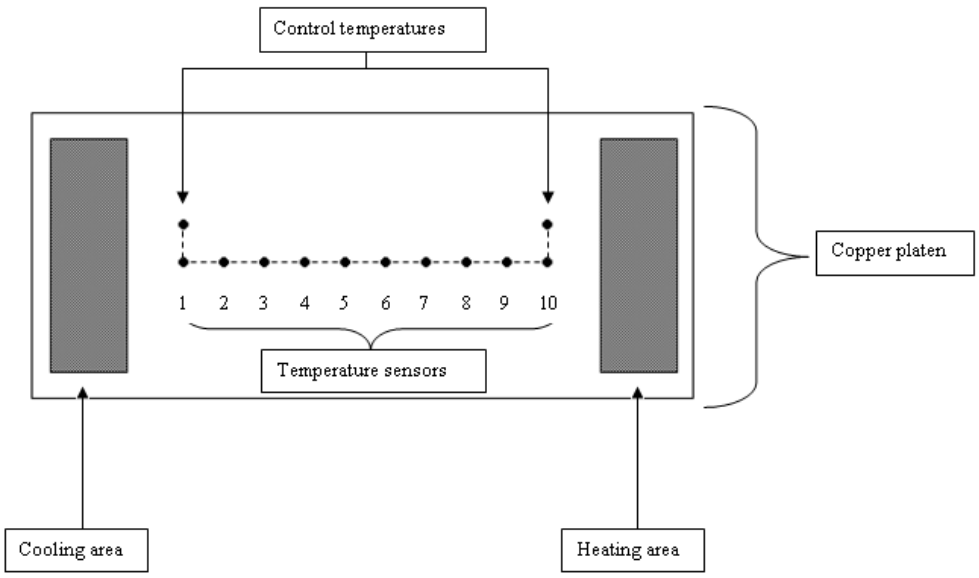


Figure 3.14: Minimum film formation temperature bar apparatus.

Linker	Triglyceride	MFFT (°C)	T*g* (°C)	M.P. (°C)
58/59	Cocoa Butter	8	-	31
	Rapeseed Oil	9	20, 21	42
	Soybean Oil	8.7	-53, -55	26, 24
60d	Rapeseed Oil	12	-54	-
	Soybean Oil	6.8	-49	23
60a	Cocoa Butter	7	-	35
	Rapeseed Oil	12	-52, -59	27
	Soybean Oil	10.6	-50, -49	23, 24
60b	Cocoa Butter	12	-	36
	Rapeseed Oil	12	-51	27
	Soybean Oil	8.2	-49	25
60c	Cocoa Butter	14	-	36
	Rapeseed Oil	8.7	-49,	26
	Soybean Oil	9	-50	23, 25

Table 3.13: Unsaturated polymer latexes, MFFT, Tg and M.P. results

Linker	Triglyceride	MFFT (°C)	T*g* (°C)	M.P. (°C)
PE**74/75**	Rapeseed Oil	8	-50	25
	Soybean Oil	7.5	-55	24
PE**71a**	Rapeseed Oil	12	-49	25
	Soybean Oil	9	-49	25
PE**71b**	Rapeseed Oil	8.7	-47	26
	Soybean Oil	9.8	-40	23
PE**71c**	Rapeseed Oil	12	-51	25
	Soybean Oil	10.6	-52	25

Table 3.14: Partially epoxidised polymer latexes, MFFT, Tg and M.P.

Linker	Triglyceride	MFFT (°C)	T*g* (°C)	M.P. (°C)
71a	Rapeseed Oil	9.8	-53	24.6
71b	Rapeseed Oil	12	-53, -55	25, 61
71c	Rapeseed Oil	12	-52, -55	25

Table 3.15: Fully epoxidised polymer latexes, MFFT, Tg and M.P.

The MFFTs observed were all shown to be between 7 and 12 °C which are all within a good range, as mentioned before with regards to indoor decorative paints.

The glass transition temperature or Tg is strongly related to the minimum film formation temperature (MFFT). These were measured using Differential Scanning Calorimetry or DSC. Figure 3.15 shows an example of a DSC curve of a control latex of pBMA, showing only a melting/softening point.

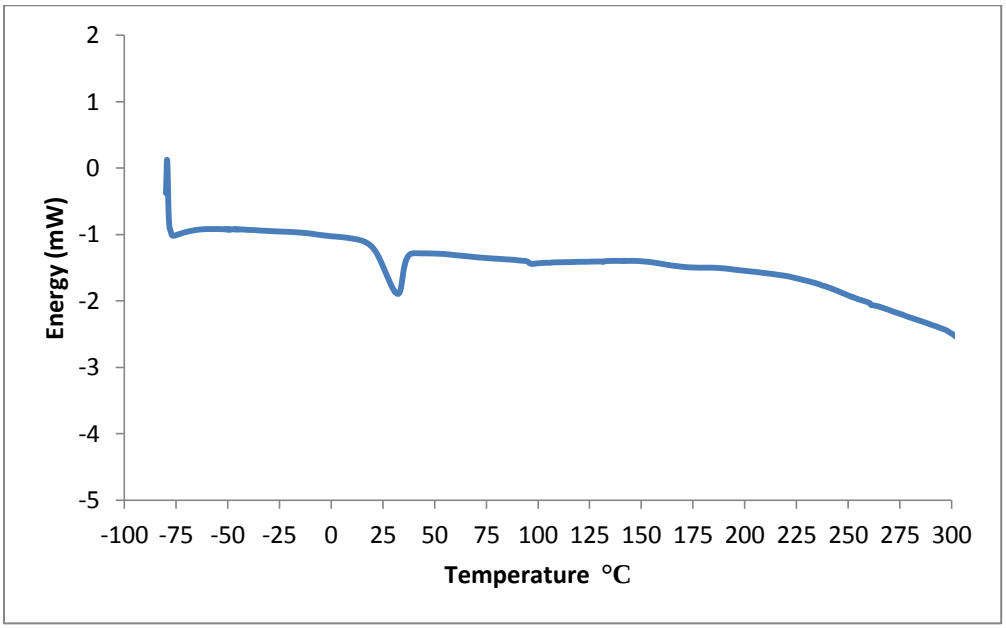


Figure 3.15: DSC curve of pBMA control latex showing a slight softening point at ~32 °C .[171]

Samples (average sample mass between 4-10 mg) were cooled to -80 °C and subsequently heated to 600 °C at a constant rate of 10 °C/min. Tg was denoted as the mid-point of the curve transition step. The film was cast on glass plates at 75 nm thickness. After drying in air at RT for 7 days a sample was prepared by cutting and folding a section of the film. The Tg for a pBMA was found to be anywhere between 21 and 28 °C,[157] Giving a clear crazed film on drying. BMA is technically known as a hard monomer. These are usually described as having a high Tg, although in this case the hard monomers Tg is actually relatively low. The vegetable oil monomers are quite soft monomers and have a Tg much lower, most likely to be somewhere in the -50 °C region (see 2.6). A copolymer between these monomers should yield a Tg somewhere between the two. With 10% of the vegetable oil monomer used, a Tg of slightly below 0 °C could be expected. Looking at all of the Tgs for the various latexes (tables 3.13, 3.14 and 3.15) the Tgs are generally appearing between -60 and -49 °C which seems extremely low given the amount of biomonomer used. In fact in most cases these Tgs are lower than those reported in Chapter 2 for the corresponding biomonomers. It is possible that with the conditions (10 ˚C/ min ramping) then the Tg of the polymers was not observed and instead were are observing the Tg of another component (e.g. the surfactant). In the latexes prepared the amount of surfactant used is quite high, the Tg for the disponil surfactant is -80 °C, which could be partially responsible for this lowering.

3.6 Effect of Increased Biomonomer Incorporation

A small study on the effects of increasing the incorporation of the biomonomer was carried out. The monomer chosen was the unsaturated rapeseed and ethylenediamine

derived monomer RS**(60a)**, (Tables 3.16-3.18). Increased biomonomer incorporation was still possible up to at least 20 wt % with clear cohesive films with good MFFTs still being attained. There is a slight decrease in the conversion with increased amounts of biomonomer, this could be due to slower propagation of polymerisation with the biomonomer with respect to BMA. Increasing amounts of biomonomer leads to lower MFFT's, and softer materials as would be expected with the incorporation of more 'soft' monomers. With regards to Tgs of these samples however, none were visible on the DSC curves. This could be due to the conditions used to obtain the results. It is possible that with a slower heat ramping that a Tg event may be visible, however time did not allow for these extra tests. Gel content was also measured and it was determined that with the incorporation of a higher percentage of biomonomer an increase in gel content was observed with 0 % for the control monomer of just BMA, 32 % for 10 % incorporation of biomonomer and up to 40 % gel content when 20 % was incorporated.

% Biomonomer	**% Conversion**			**Particle Size (nm)**	**PDI**
	BM	**BMA**	**Total**		
10%	91	95	94.6	177	0.04
15%	86	92	91.1	175	0.06
20%	81	91	89	194	0.08

BM = biomonomer, BMA = butyl methacrylate

Table 3.16: % solids, conversion and particle size comparison when varying the % biomonomers used

% Biomonomer	MFFT (°C)	Tg (°C)	M.P. (°C)	Gel content
10%	12	-52, -59	27	30 %
15%	8	-	36	35 %
20%	7 (visual change at 12)	-	37	39 %

Table 3.17: MFFT, Tg and M.P. comparison when varying the % biomonomers used

% Biomonomer	Hardness	Film
10%	23	Clear films, slight mottling and bloom over time
15%	18	Film spread out. Clear. Some cracks and visible (air?) rings.
20%	13	Film spread out. Clear. Some cracks.

Table 3.18: Hardness and film comparison when varying the % biomonomers used

3.7 Yellowing Tests

One major aim of this project was to try and reduce the amount of yellowing that occurs in paint films over time, as this was one of the disadvantages that was found

with alkyd paints.[172] It has been suggested that this discolouration could come from by-products of oxidative cross-linking that occurs between the alkenes in fatty acid chains that are found in these kinds of coatings.[173]. This mechanism is used to form films in drying oils (1.4.1.1) and alkyd coatings (1.4.3).[174,175] There are a number of approaches that can be employed to test the yellowing of films.[176] One approach is to use a solar simulator at an enhanced level to expedite the yellowing process. In our study, the samples were cast onto microscope slides and allowed to dry overnight at room temperature to give a dry clear film. The samples were then photographed and placed inside an oven at 50 °C and were removed at two day intervals to assess visually whether yellowing had occurred.

Four latex samples containing either 10% or 20% renewable oil monomers, were prepared and cast into films on microscope slides. Ethylenediamine was chosen and the amount of unsaturation in rapeseed oil was varied (unsaturated 20% RS**(60a)**, unsaturated 10% RS**(60a)**, partially epoxidised 10% PERS**(71a)**) to give three samples which were compared to unsaturated cocoa butter CB**(60a)** (also with an ethylenediamine linker). Initially we analysed the films every two days for a total period of twelve days, (Figure 3.16).

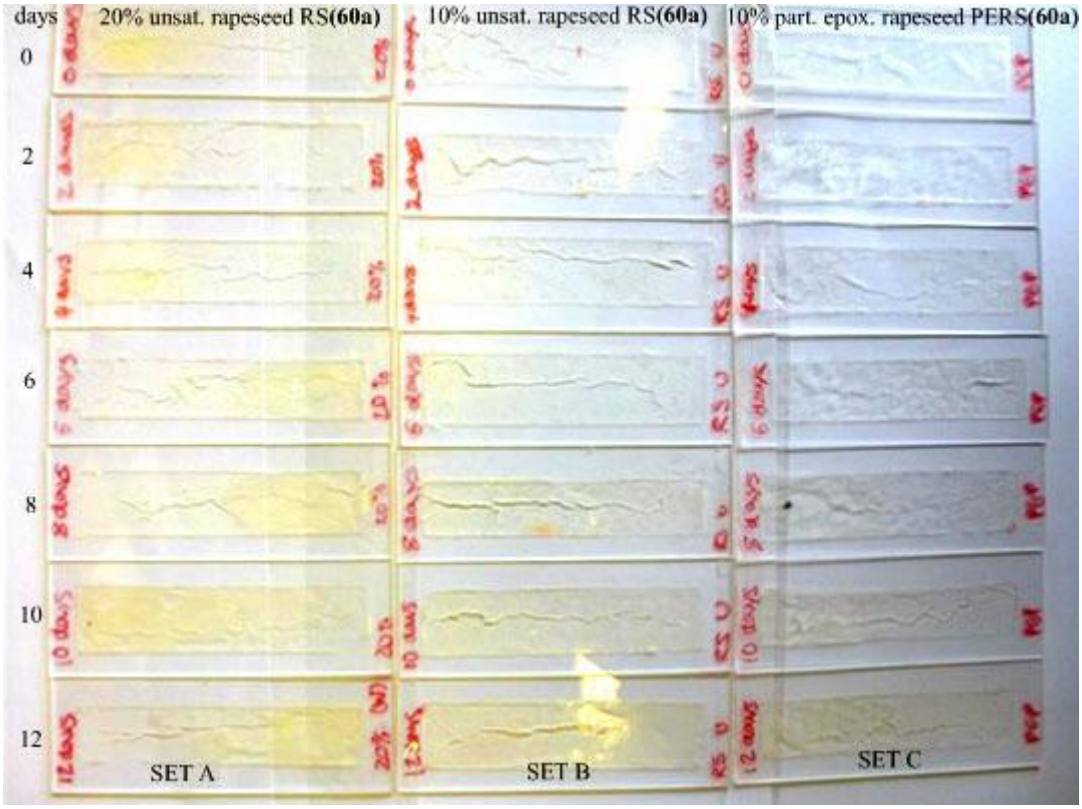
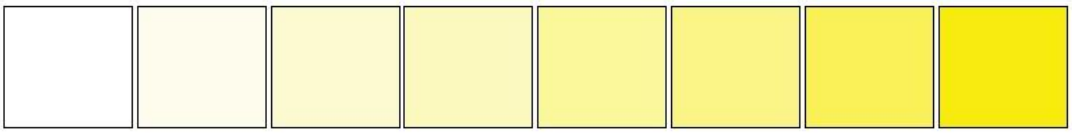


Figure 3.16: Photo showing latex film samples incorporating unsaturated rapeseed oil, partially epoxidised and unsaturated rapeseed oil with 20% biomonomer. All shown at 0, 2, 4, 6, 8, 10 and 12 days

It was found that all of the slides made light yellow, or colourless films upon drying overnight, with the sample incorporating 20 % unsaturated rapeseed biomomomer (SET A) showing the most yellowing, and the partially epoxidised 10% PERS**(71a)** being completely colourless. Over the twelve day period, it was observed that each sample became more yellow in colour, however to differing degrees. UV/Vis spectroscopy for quantitative analysis was trialled, however this was unsuccessful. Instead, a yellowing scale was used from 0 to 7 to visually assess the latex films, with 0 being clear and 7 being yellow, (Figure 3.17). Table 3.19 shows the change in colour of each sample seen over 150 days, using the yellowing scale.



0 1 2 3 4 5 6 7

Figure 3.17: Yellowing scale for use with latexes

Sample	Yellowing (using colour scale Figure 3.17)							
	0 d	2 d	4 d	6 d	8 d	10 d	12 d	150 d
10% RS**(60a)**	2	2	2	2	3	4	5	6
PERS**(71a)**	0	0	0	1	1	2	2	2
20% RS**(60a)**	3	3	3	4	4	5	5	6
CB**(60a)**	2	2	2	2	3	3	4	7

Table 3.19: Yellowing of latex samples at 0, 2, 4, 6, 8, 10, 12 and 150 days.

It was observed that although the sample containing 20 % biomonomer (SET A) started slightly more yellow than the sample containing only 10 % biomonomer (SET B) (SET A = 3 and SET B = 2), over the course of twelve days, they both yellowed to the same end point, reaching 5 on the yellowing scale. On removal of some of the double bonds *via* epoxidation, it was observed that the yellowing of the films was greatly decreased (SET C), changing from 0 to 2 over the course of twelve days. To see the colour change in samples more clearly, one slide of each sample was kept in the oven for considerably longer (150 days). Figure 3.18 shows the colouring of unsaturated RS**(60a)** (SET E) and partially epoxidised PERS**(60a)** (SET F) latex films after 150 days. CB**(60a)** (SETD) is also shown for comparison. After 150 days, SET D reached 7 on the yellowing scale (Figure 3.17), SET E reached 6 and SET F (the partially epoxidised 10% PERS**(71a))** only reached 2, giving a positive result for removal of unsaturation with regards to yellowing.

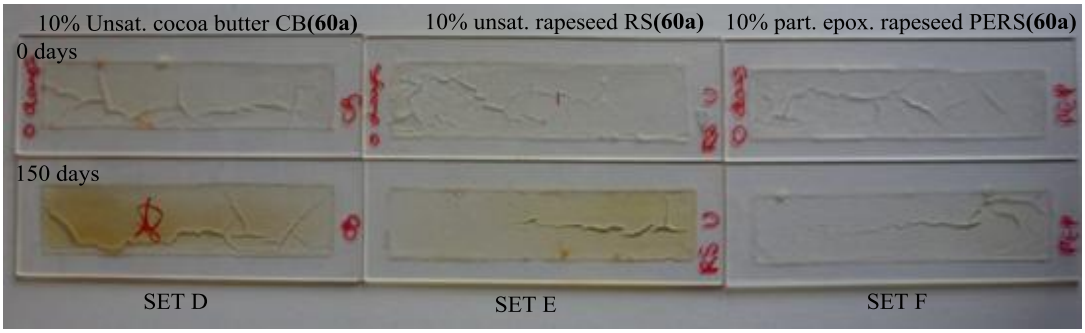


Figure 3.18: Photo showing cocoa butter latex, unsaturated rapeseed oil latex and partially epoxidised rapeseed oil latex all at 0 days and 150 days.

Interestingly, considerably more yellowing was observed for the unsaturated cocoa butter latex, than for the rapeseed derived latex. This is contrary to expectation, as there are less residual alkenes present in the cocoa butter latex. This suggests that the level of residual alkenes is not the complete picture in causing yellowing.

3.8 Summary and Conclusions

Overall it was found that it was possible to prepare water based latex systems of the diamide based biomonomers **(60a-c)** even though the monomers were low melting point solids instead of viscous oils, such as the monomers of **(58/59)** and **(60d)**.

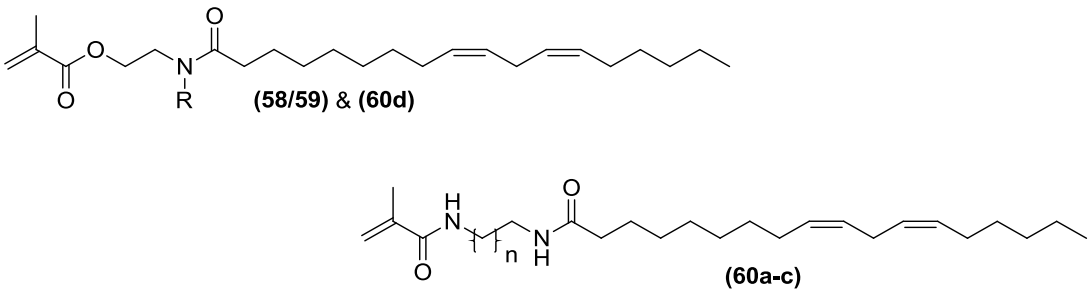


Figure 3.19: Diamide and ethanolamine derived monomers

Some difficulty was found when initially trying to incorporate the biomonomers into the initial monomer emulsion. Trouble was encountered especially with the cocoa butter based monomers (CB), as gelation would occur on cooling, this could be due to their highly saturated nature which might allow for more close packing of chains and better H-bonding within the linking amide chains. Epoxidation of the double bonds also seemed to hinder the incorporation of the biomonomers into the latexes with lower conversions. Epoxidation also affected the brittleness of the films making them slightly more flexible and this was thought to be due to the epoxy chains acting in the role of plasticiser. Increasing the amount of biomonomers in the formulation caused a lowering of conversion, and the formation of a softer latex that was less stable to yellowing with lower MFFT's. It was found that partially epoxidised materials underwent less yellowing over time than fully unsaturated materials, but that cocoa butter derived materials underwent the most yellowing over time. Thus the hypothesis that yellowing is due to residual unsaturation in the latexes cannot be the whole picture.

Unfortunately due to little data given in the original literature by Thames[137] as to the physical properties of the latexes prepared from **(58/59)** and **(60d)**, comparison of their monomers with ours was done by ourselves. Preliminary tests seem to indicate similar properties to our own biomonomers (see Tables 3.6-3.15). Clear cohesive films, could be produced with both classes of latexes, with comparable MFFTs and degrees of hardness.

4.0 Chapter 4 Biopolyols in Polyurethane Synthesis

This chapter will concentrate on the synthesis of polyols derived from triglycerides and their use in the preparation of polyurethanes.

4.1. Polyurethane Introduction

Although a relatively new type of polymer, polyurethanes (PU's) have become one of the most abundantly used polymers around; this is likely due to their versatility. Being first reported in 1937 by Bayer,[177] they are most commonly used in both flexible and rigid foams but can also be used in almost all polymer applications, including elastomers, coatings and adhesives among many others due to the extremely varied properties.[178] Flexible foams can be used in packaging, bedding and automotive interiors including headrests, dashboards, roof liners and seating, whereas rigid foams are used more for insulation. Polyurethane based elastomers can also be used in many applications ranging from footwear to print rollers. It was estimated that in 2005 the world consumption of PUs was 8.8 million tons.[179] As with coatings, the first PUs were derived from petrochemicals.

PUs are formed by reaction of a hydroxyl group with an isocyanate group forming a urethane linker as shown in Figure 4.1.

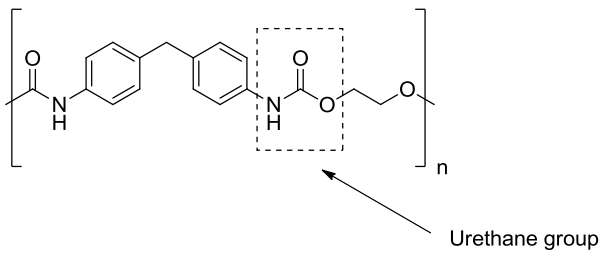


Figure 4.1: Generic polyurethane, highlighting the urethane linker.

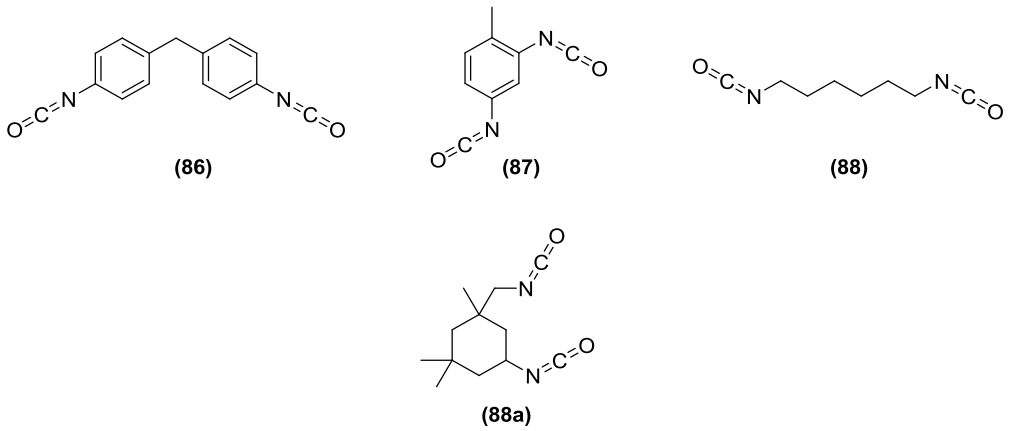
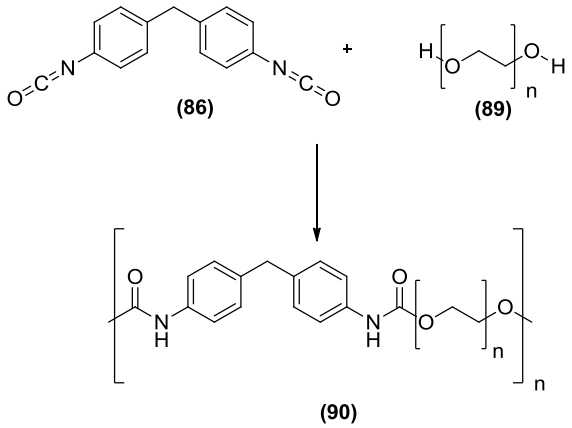


Figure 4.2: Common Diisocyanates MDI (86), TDI (87) HDI (88) and IPDI (88a).

Usually a petroleum derived polyol such as a polyethylene glycol is reacted with a petroleum derived diisocyanate such as MDI **(86)** to give a polyurethane (Figure 4.3). A number of different diisocyanates are available and they can be both aromatic and aliphatic in structure. Common diisocyanates include 2,4-toluene diisocyanate (TDI) **(87)**, 1,6-hexamethylene diisocyanate (HDI) **(88)** and isophorone diisocyanate **(88a)**, (Figure 4.2). The chemical structure of the polyol and the diisocyanate will determine the mechanical and thermal properties of the PU. Structurally a PU can be separated into two components, namely a hard or rigid segment (mainly formed from the urethane link) and a soft or flexible segment (mainly made up by polyol chain).[180] The soft segment imparts flexibility to the polymer. Flexible materials are made from large polyols (molecular weight typically between 3-6 KDa) with a low number of hydroxyl groups per molecule (typically 2-3). These give low cross-linking densities and flexible structures. Alternatively, stiffer and more rigid PU's are normally prepared by smaller polyols (typically 0.3-1.0 KDa) with a higher number of hydroxyl groups a molecule (3-8). These have

greater cross-linking densities and the polymer chains are less able to move imparting rigidity.



Scheme 4.3: Synthesis of polyurethane from MDI and polyol

Recently extensive research has been done to replace the commercially available polyols with renewable based polyols. Saccharides[181] or their biotransformation products were originally investigated to replace petrochemical based polyols with a renewable source. One such example includes 1,3-propanediol **(91)** (Figure 4.4), which Dupont synthesised from corn for use as a commercial diol.[182] Roquette also proposed the use of sorbitol **(92)** (Figure 4.4), which can be produced from the hydrogenation of glucose and used in Neosorb®.[181]

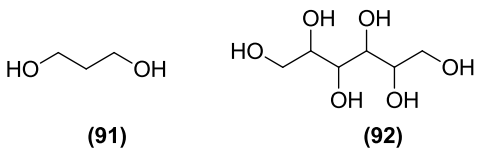


Figure 4.4: 1,3-propanediol as obtained from biomass and Sorbitol, used in Neosorb®

However, due to their relatively small molecular weight they resulted in low renewable content in the subsequent polyurethanes, so vegetable oils with larger molecular weights were investigated. Most vegetable oils do not contain hydroxyl functionality and so they would have to be chemically modified to include the desired hydroxyl functionality. A number of studies have been carried out by Petrovic and co-workers[44,45,183-185] into the use of polyols derived from soybean oil for use in polyurethanes. They have ring-opened epoxidised soybean oil **(6)** with a variety of nucleophiles to give a range of hydroxylated vegetable oils.[45,181,183]

Other reactions of triglycerides include hydrolysis, ring-opening, glycerolysis, hydroformulation /reduction, hydrogenation and ring opening polymerisation. Some of his earlier work however looked into the use of castor oil as a basis for PU's.[186] In this study the temperature of mixing and curing was investigated, looking at RT, 90 °C and 120 °C. As castor oil contains naturally occurring hydroxyl groups, castor oil was used with no further modification.

There have been many polyols developed for commercial uses by companies over the last few years. One such polyol developed from epoxidised triglycerides **(4)** for commercial use is Jeffadd™ B650. This was developed by Huntsman company and involved the use of epoxidised soybean oil **(4)** containing between 2 and 6 epoxides; this was subsequently reacted with aminoalcohols for 4 h at 120 °C. The amines reacted with the oxirane rings to form a ring-opened product **(93)**. In addition to this, reactions took place between the amine and the carbonyl of the glyceride to produce shorter chained fatty amide polyols **(94)**. These polyols have been used in a number of different applications including rigid foams, coatings and especially low-density polyurethane spray applications due to their water solubility.[187]

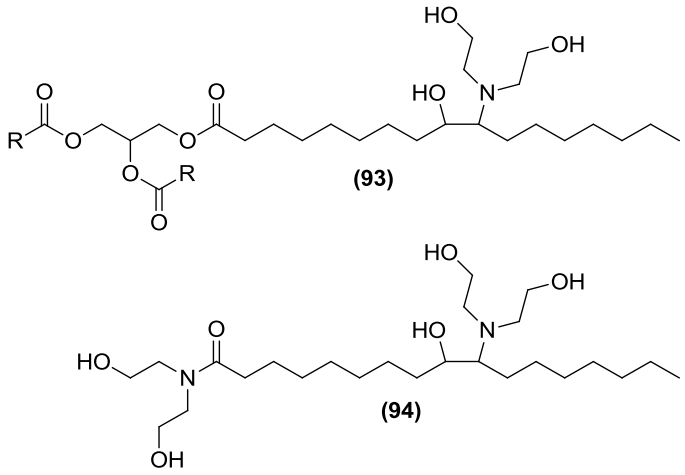


Figure 4.5: Polyols (93, 94) produced by Huntsman company using amines to ring open epoxidised soybean oil

Both Cognis and BASF have a number of vegetable oil based polyols known as Sovermol®. These are produced *via* epoxidation, ring-opening using an alcohol followed by transesterification using the same alcohol used in the ring-opening procedure, (Figure 4.6).[188]

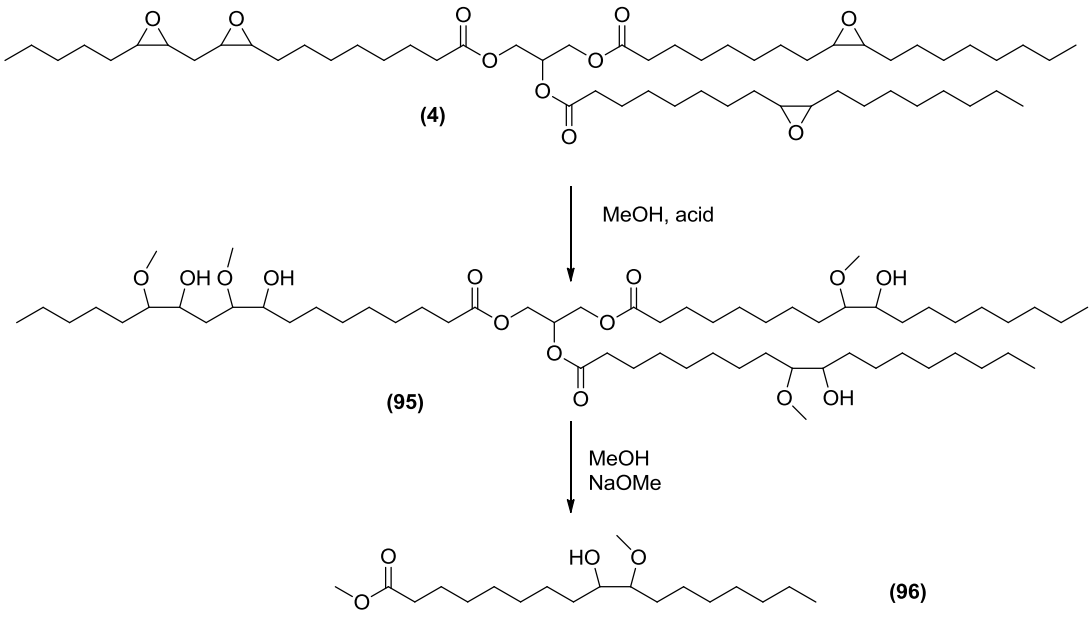


Figure 4.6: Example where epoxide is ring opened and then transesterified both with CH_3OH

Bayer developed a biobased polyol, again based on soybean oil **(1)** *via* epoxidation **(4)** followed by hydrogenation giving secondary hydroxyl groups **(97)**. These are then ethoxylated by an alkylene oxide and a metal cyanide giving a primary hydroxyl functionality **(98)** and are used in both flexible and rigid PU foams.[189]

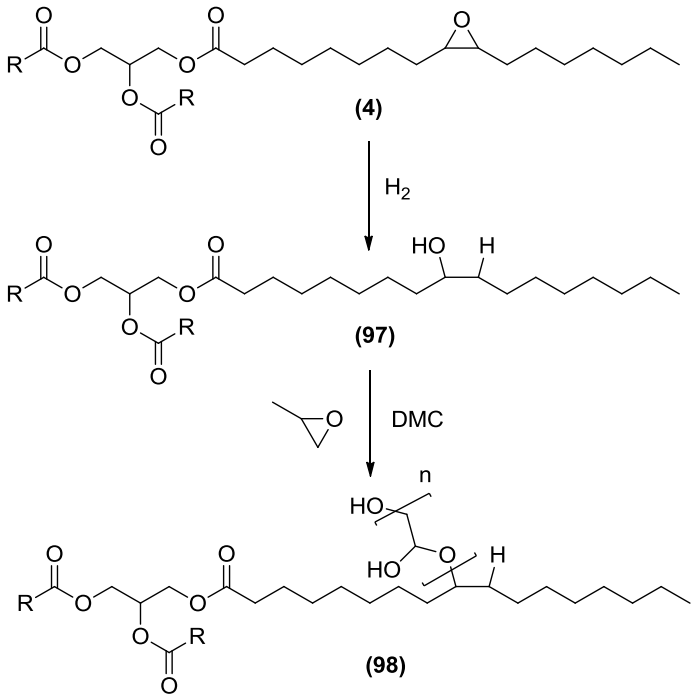


Figure 4.7 Example of polyol synthesised *via* hydrogenation of epoxide followed by ethoxylation

Finally, Biobased Technologies have developed a number of different polyols including Agrol® (**99**) which is based on soybean oil and made from a two-step process, firstly involving epoxidation of the vegetable oil alkene groups with a peracid followed by ring opening of these oxirane rings, using the acid by-product from the epoxidation step.[190] Agrol® Diamond **(100)** was then developed which took the soybean based Agrol® polyols and carried out an aminolysis reaction to produce smaller highly functionalised polyols.[191] These polyols are often used in the preparation of low density rigid PU foams with a compressive strength of 48 psi.

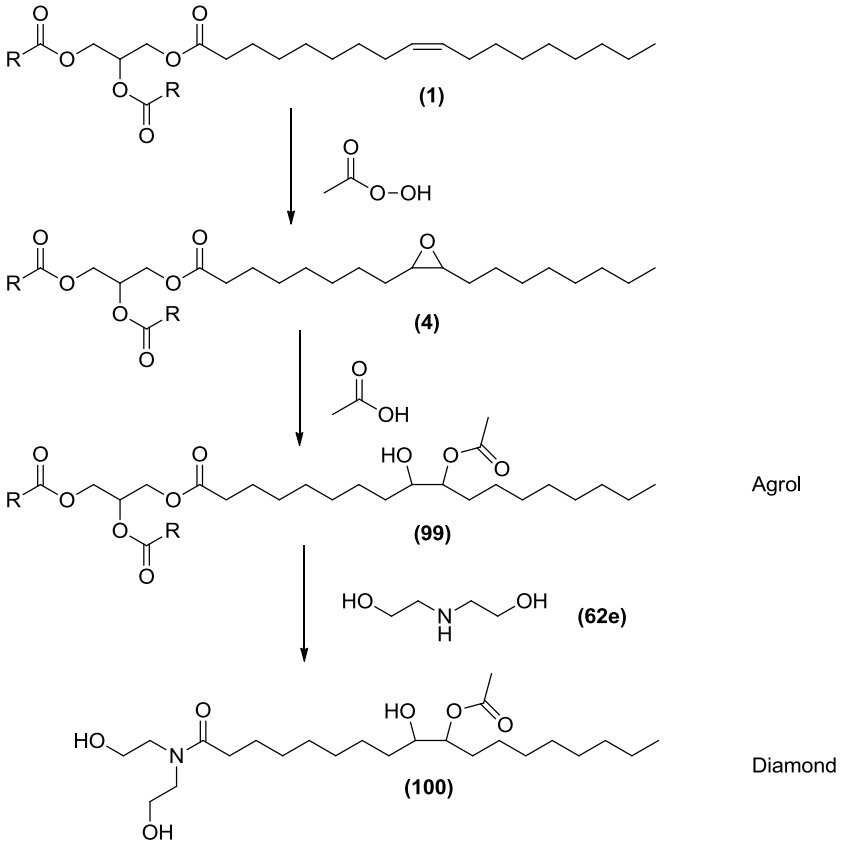


Figure 4.8: Synthesis of Agrol and Diamond polyols made by Biobased Technologies

As well as modifying the double bond to introduce functionality capable of use in polyurethanes, the functionalisation of the ester carbonyl group should not be ignored. One such example includes the use of glycerol as mentioned in section 1.3.2.1, this yields both mono- **(27)** and diglycerides **(28)** that can then be reacted with diisocyanates.[192-194]

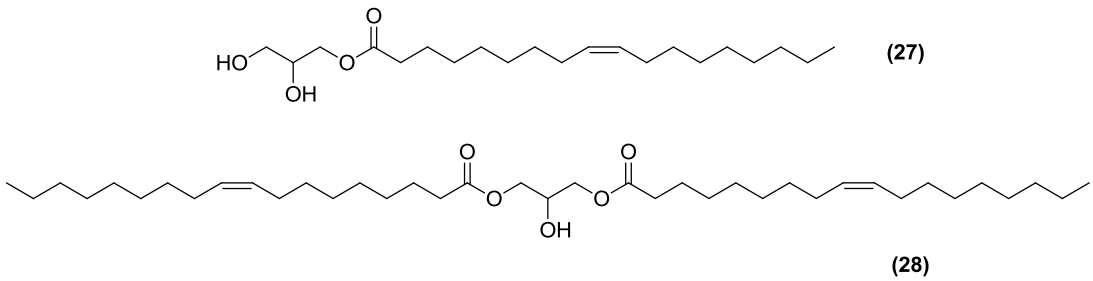
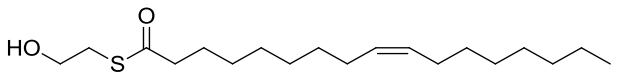


Figure 4.9: Mono- (27) and diglycerides (28)

Work by Campanella *et al* [192] produced monoglycerides from soybean oil similar to **(27)** that were used to prepare PU foams. Tensile strength of these PU samples ranged from 1.7 – 2.3 MPa, with Tgs ranging from -10 to 12 °C with percentage elongation reaching 76 %.

Amidification can also be useful; it can be used on both triglycerides and straight fatty acids.[195] Thioesterification is another process that could be used; similar to the amidification process this would introduce a thiol function, for example using mercaptoethanol (Figure 4.10). Other examples include, reduction, azidation and lactone synthesis followed by ring opening.[196]



(101)

Figure 4.10: Example of thioesterified triglyceride oil

4.2. Polyurethane Synthesis

Work has been done previously into the effect of isocyanate group on the properties; with aromatic triisocyanates affording the highest densities, tensile strength, modulus and glass transition; with the aliphatic diisocyanates giving rubbery PUs and lower tensile strength.[197] Although there is a large range of isocyanates available, MDI was used in this chapter as it is one of the most common isocyanates used and is readily available.

It has been shown before that polyols made from vegetable oils **(1)** and diethanolamine **(63e),** namely **(30)** and **(102)**, can be utilised in the synthesis of polyurethanes.[181,198] One example investigated the use of epoxidised palm oil based

epoxidised diethanolamines in the preparation of rigid foams.[198] During the earlier chapters of this thesis we have prepared a range of mono-, di- and polyhydroxylated materials from vegetable oils (e.g. RS**(30),** RS**(61c)**) and we wished to examine if they could be used to make polyurethanes. Specifically we decided to compare the polyurethanes produced from reacting MDI with the range of polyols prepared by the aminolysis of triglycerides **(1)** with **(63e)** and sodium methoxide as seen in section 2.4.1. These could be compared to those of similar structure (e.g. those from Lee *et al*)[198]

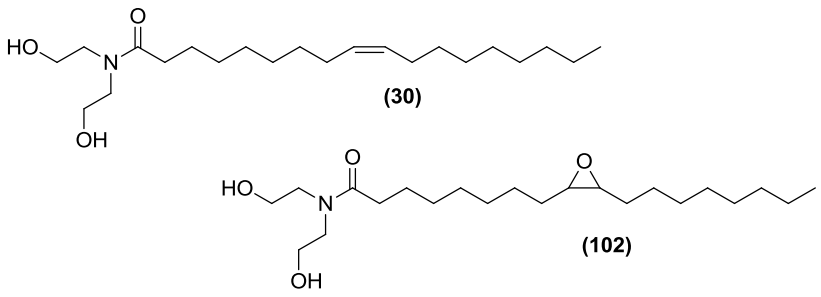
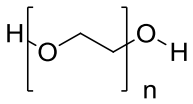


Figure 4.11: Unsaturated and epoxidised fatty amides

Recent work in our group had shown that the properties of polyurethanes from vegetable oils can be tailored by the addition of polyols such as butane diols and PEGs **(89)**. We also wished to determine how the change from an alkene to an epoxide functionality in the chain would affect properties. In theory, polymerisation of the epoxidised monomers **(102)** would give a PU with a potential epoxide group to allow cross-linking during a second step. A small library of diols were prepared using cocoa butter and rapeseed oil as the base triglycerides **(1)**. Those based upon cocoa butter would have mainly saturated chains, while those from rapeseed would have mainly unsaturated sidechains. Thus the differences in properties of PU's from epoxidised and unepoxidised cocoa butter should be far less than the corresponding

rapeseed derived materials. Target molecules were prepared by transamidation of the vegetable oils using the procedure described in section 2.4.1 followed by reaction of residual alkenes with mCPBA.



(89)

Figure 4.12: General structure of PEG

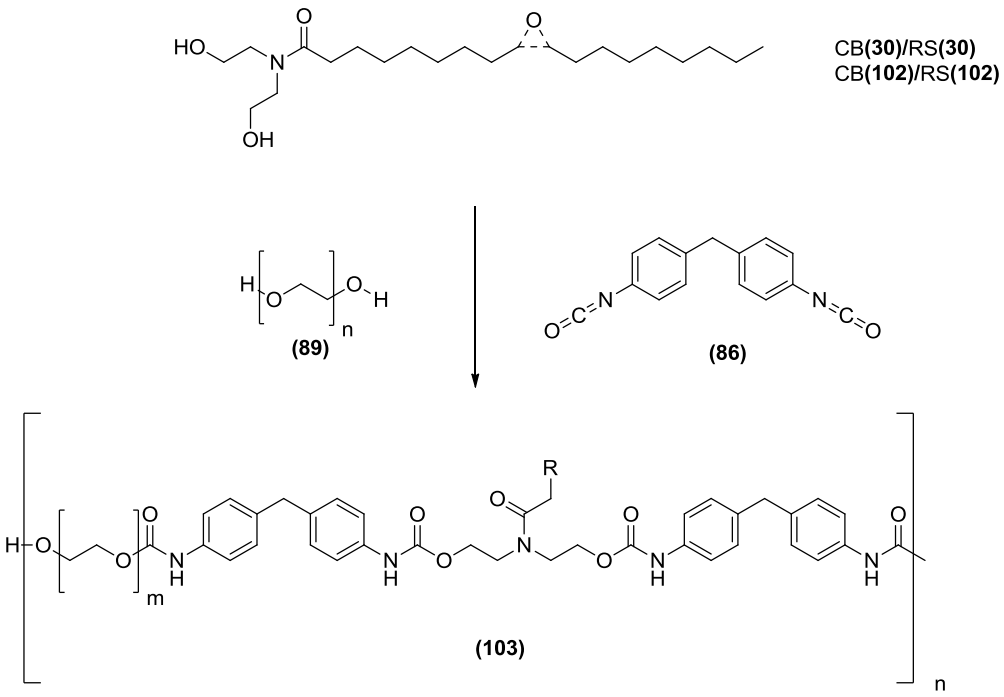


Figure 4.13: General scheme for reaction of diol with MDI and PEGs

With the 4 diol feedstocks in hand (CB**(30)** = cocoa butter unepoxidised, CB**(102)** = cocoa butter epoxidised, RS**(30)** = rapeseed unepoxidised, RS**(102)** = rapeseed epoxidised) in hand they were each mixed 1:1 with MDI in chloroform at reflux for 24 h under a nitrogen atmosphere in chloroform to form a polyurethane (Figure 4.13).

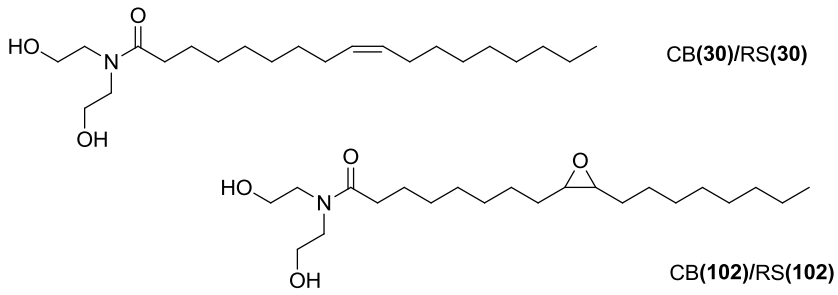


Figure 4.14: Unsaturated and epoxidised diols derived from cocoa butter (CB(30) and CB(102)) and rapeseed oil (RS(30) and RS(102))

The solvent was then removed *in vacuo* and the polymer poured into a pre-greased mould and heated in an oven at 50 °C for 24 h to allow for curing. In order to assess the effect of additional hard segments each of the four feedstocks was reacted with an additional equivalent of either butane diol, PEG 400 or PEG 3350. Each polyol was reacted in a 0.5:0.5:1 ratio of polyol to commercial polyol to MDI, or a 1:1 ratio when prepared without the commercial diol.

Polyol	**PEG/BD**	**Physical properties**	Pull apart by hand?
CB**(30)**	N/A	Hard brittle solid	Yes
CB**(30)**	BD	Hard brittle solid	Yes
CB**(30)**	PEG400	Soft flexible solid	Yes
CB**(30)**	PEG3350	Hard brittle solid	Yes
CB**(102)**	N/A	Hard brittle solid	Yes
CB**(102)**	BD	Hard brittle solid	Yes
CB**(102)**	PEG400	Soft flexible solid	Yes
CB**(102)**	PEG3350	Hard brittle solid	Yes

Table 4.1: Physical properties and strength of cocoa butter PU samples

Polyol	**PEG/BD**	**Physical properties**	Pull apart by hand?
RS**(30)**	N/A	Hard brittle solid	Yes
RS**(30)**	BD	Hard brittle solid	Yes
RS**(30)**	PEG400	Soft flexible solid	Yes
RS**(30)**	PEG3350	Hard brittle solid	Yes
RS**(102)**	N/A	Hard brittle solid	Yes
RS**(102)**	BD	Hard brittle solid	Yes
RS**(102)**	PEG400	Soft flexible solid	Yes
RS**(102)**	PEG3350	Hard brittle solid	Yes

Table 4.2: Physical properties and strength of rapeseed PU samples

4.3. Thermal and Swelling Tests

DSC and TGA experiments were run on all PU samples. The percentage swelling was also calculated, with regards to solvent, in this case toluene and water. The percentage swelling was measured by immersing the pre-weighed samples into vials of either water or toluene and left for 48 hours, upon which the samples were dabbed dry and their new weights measured. The results are shown below in Tables 4.3 and 4.4.

Polymer	PEG/BD	Cross-link density (mol/cm^3) $x10^{-4}$	Swell % (water)
CB**(30)**	N/A	17.2	1.8
CB**(30)**	BD	*	10
CB**(30)**	PEG400	46.3	17.7
CB**(30)**	PEG3350	*	50.1
CB**(102)**	N/A	*	1.5
CB**(102)**	BD	101.1	6.7
CB**(102)**	PEG 400	*	14.3
CB**(102)**	PEG3350	80.2	48.2

* = Some breakdown of the polymer is observed

Table 4.3: Results of tests on cocoa butter derived polyurethanes

Polymer	PEG/BD	Cross-link density (mol/cm^3) $x10^{-4}$	Swell % (water)
RS**(30)**	N/A	*	14.3
RS**(30)**	Butanediol	14.1	10.5
RS**(30)**	PEG 400	20.1	15.3
RS**(30)**	PEG 3350	19.3	45.5
RS**(102)**	N/A	28.6	0.8
RS**(102)**	Butanediol	27.2	1.0
RS**(102)**	PEG 400	31.1	16.2
RS**(102)**	PEG 3350	69.9	26.4

* = Some breakdown of the polymer is observed.

Table 4.4: Results of tests on rapeseed oil derived polyurethanes

Unfortunately a Tg was unable to be discerned from the DSC. This is not unusual in vegetable oil based polyurethanes and as the amount of hard segment increases Tg can become very broadened, but also may be due to the heating method. Zlatanic *et al* determined that Tg can be decreased substantially in vegetable oil PU's as the dangling chains can act as plasticizers.[199] There were also no significant melting points observed on the curves. This suggests a hard, cross-linked polymer.

Initial results showed that these polyols produced glassy very brittle PU's when reacted without PEG or butanediol in a 1:1 ratio with MDI in 100 mL of chloroform. On addition of a second simple diol some change in physical appearance was observed. Butanediol caused further brittleness to occur, although this is not surprising as it increases the amount of hard segment in the overall material. The butanediol materials were quite opaque, whereas PEG 400 gave a much more visually transparent and flexible material (Figure 4.15). The use of PEG 3350 gave a PU somewhere between that of the PEG 400 and butanediol, with more opaque looking polymer, with much less flexibility than the PEG 400, but being slightly less brittle than the butanediol.

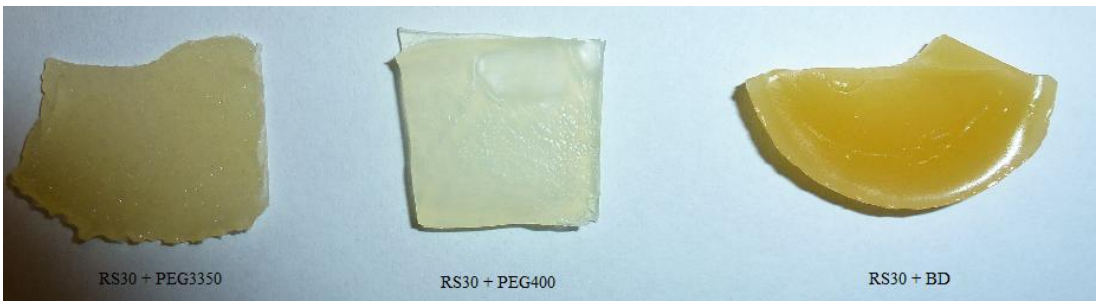


Figure 4.15: The difference in physical appearance of RS30 with commercial diols (BD, PEG400 and PEG3350)

Varying the ratio of PEG to the biopolyol was briefly investigated, by looking into the properties of polyurethanes produced using a 1:3 PEG to biopolyol ratio. This was carried out on the epoxidised cocoa butter and epoxidised rapeseed oil diols with PEG 3350 being the commercial diol of choice. Initial results showed an opaque quite brittle polymer.

The swelling tests showed that when exposed to water the uptake increased when higher weight commercial diols were copolymerised into the plastics. When no commercial diol is incorporated the swelling is generally between 0.5 and 2 %. When 1,4-butanediol is incorporated the swelling increases to between 1 and 10 % and with PEG 400 increases again to between 14 and 18 %. However when PEG 3350 is incorporated you see a substantial increase in swelling to between 26 and 50 %. This is likely due to the increased 'space' between any cross-links and chains due to the length of the PEG. Swelling in water may be important for maximising the potential for biodegradability of materials, although formal biodegradability tests were not carried out to confirm this. This is because non-cross-linked materials have a better accessibility to enzymes than do highly cross-linked materials. Samples were exposed to toluene to help determine the cross-linking density of PU's; The Flory-Rehner equation[200] (see Appendix C) can then be used to calculated the molecular weight between cross-links that can subsequently be used to give the cross-link density, which are shown in Tables 4.3 and 4.4. The first surprise is that cross-linking densities are relatively high. For the reaction of diol **(30)** with MDI a linear polymer with negligible cross-linking density would be expected. For such cross-linking to occur indicates that significant allophanate and biuret formation is occurring under the reaction conditions. Allophanate formation occurs due to the high reactivity of the isocyanate group reacting with the polymer urethane linkage

and is more likely to occur when a slight excesses of diisocyanate is used and at temperature above 60 ˚C. Biuret formation can occur if the original polyol samples contain low levels of water (due to the low molecular weight of H_2O with respect to the vegetable oil polyol small weight amounts become significant on the molar stoichiometry). This leads to ureas and consequently biurets.[201] Another important observation is that cross-linking densities for epoxidised monomers **(102)** are generally higher than for the corresponding unsaturated derivatives **(30)**,RS**(30)**/BD = 14.1 x 10^{-4} mol/cm^3 vs RS**(102)**/BD = 27.2 x 10^{-4} mol/cm^3, RS**(30)**/PEG3350 = 27.2 x 10^{-4} mol/cm^3 vs RS**(102)**/PEG3350 = 69.9 x 10^{-4} mol/cm^3 this suggests that further cross-linking is occurring *via* the epoxide group under the reaction conditions.

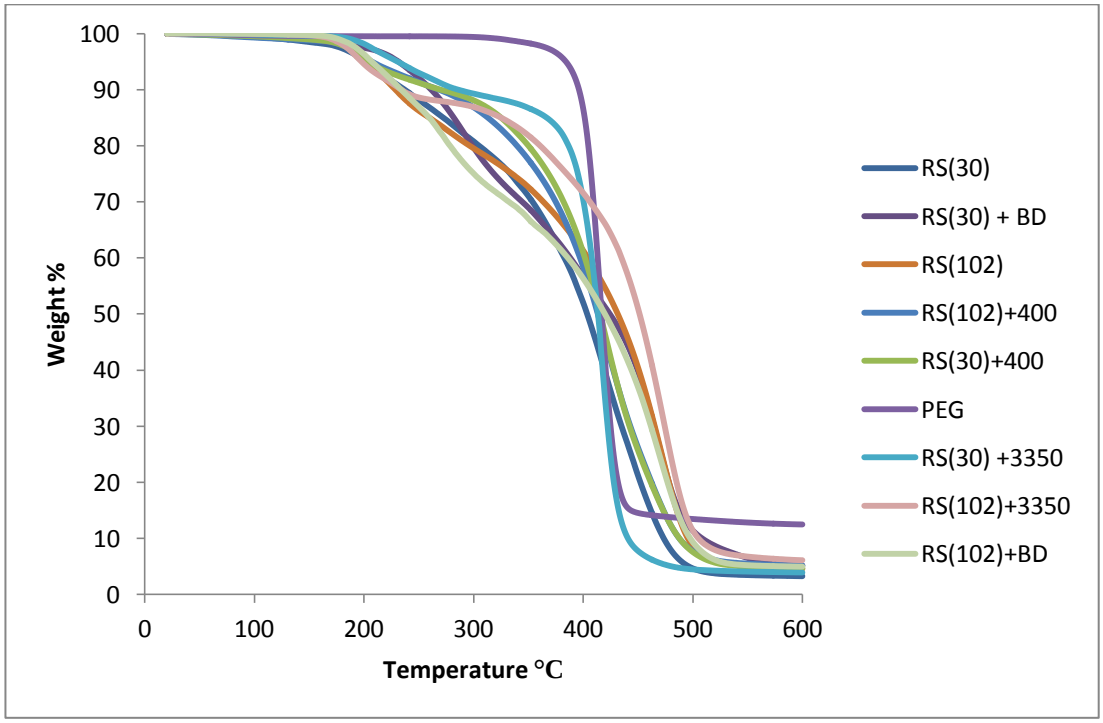


Figure 4.16: TGA analysis of RS(30)/RS(102) PU with and without hard segments and PEG separately.

TGA, (Figure 4.16) shows the thermal degradation of PU samples prepared from both RS**(102)** and RS**(30)**, with BD, PEG400, PEG3350 and without commercial diol. The PU have 2 main degradation steps; one at about 200 °C with the second at about 400 °C. This is similar to results found by Lee *et al* [198] when preparing PU foams from similar diols. This degradation is likely to correspond to the breaking of the urethane links. Notably this mass loss is not seen in the PU prepared from just PEG which just has one degradation point at 400 °C. In general the epoxidised derivatives **(102)** fully decompose at slightly higher temperatures than the unsaturated derivatives **(30)** with the latter showing the two main degradation points and the former exhibiting a smoother curve. All polymers start to degrade at roughly the same temperature < 200 °C.

4.4. Tensile Testing

A small selection of these polyurethanes were taken on for tensile testing. This method of analysis allows you to test the effects of stress and strain on the samples by subjecting them to uniaxial tension until breakage or failure is observed. From this we were able to discern the ultimate tensile strength, so the ultimate amount of stress the sample can be subjected to. The stress and strain can be plotted against each other to give a stress-strain plot which can allow us to work out the Young's modulus, which measures the stiffness of an elastic material. The samples suitable for this testing were moulded into a 'dog-bone', named due to its shape (Figure 4.17). This means it has 2 shoulders and a 'gauge' section which is a standard length. This gauge section is slightly narrower than the grip section so that deformation and

failure can occur here, with the grip section being bigger to allow for gripping by the machine.

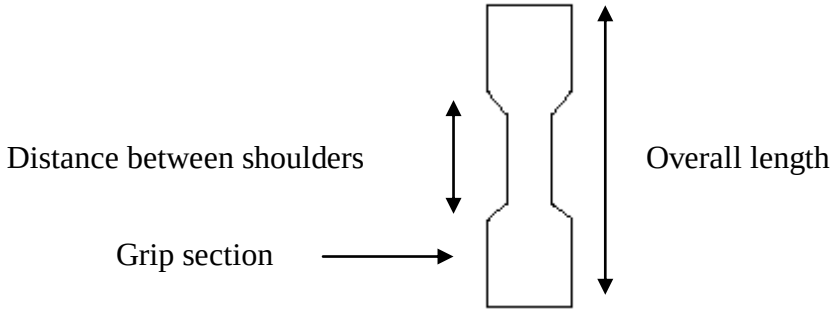


Figure 4.17: Schematic of test specimen

'Dog-bone' samples were prepared of 5 polyurethanes (5 samples for each PU), and tested using the above technique, where stress-strain data was collected and the Young's modulus calculated for each. Only 5 were chosen due to the brittle nature demonstrated by the majority of the samples making both casting or templating of test specimens a challenge. All mechanical testing was carried out using an Instron 5800 universal testing machine using dog-bones with a 12 mm 'gauge' length and 7 mm gauge width with a 47 mm total length.

Sample	Breakpoint			Young's modulus MPa	Cross-link density x10^{-4} (mol/cm^3)
	Stress (MPa)	Strain (MPa)	Elongation (%)		
CB**(102)**/PEG3350	4.58	0.05	4	115.3	80.2
RS**(102)**/PEG3350	1.39	0.03	4	52.7	69.9
RS**(102)**/PEG400	0.21	0.74	125	5.1	31.1
RS**(102)**3350(0.5:1.5:2)	1.38	0.04	4	30.5	66.5
CB**(102)**3350(0.5:1.5:2)	1.42	0.01	4	40.3	65.3

Table 4.5: Table comparing the stress-strain data from polyurethane samples

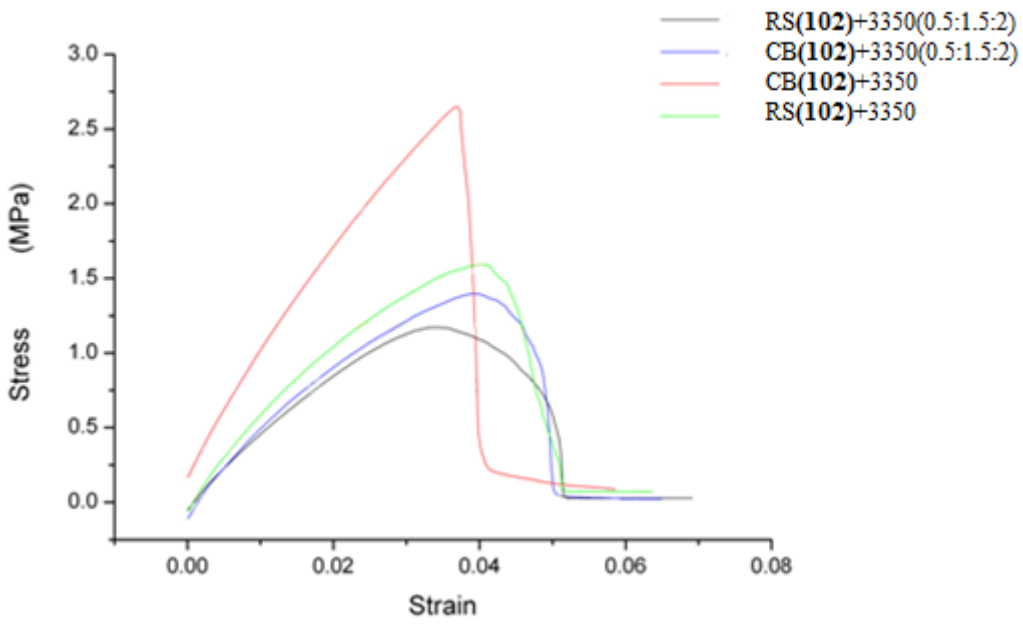


Figure 4.18: Stress strain curve of PU samples

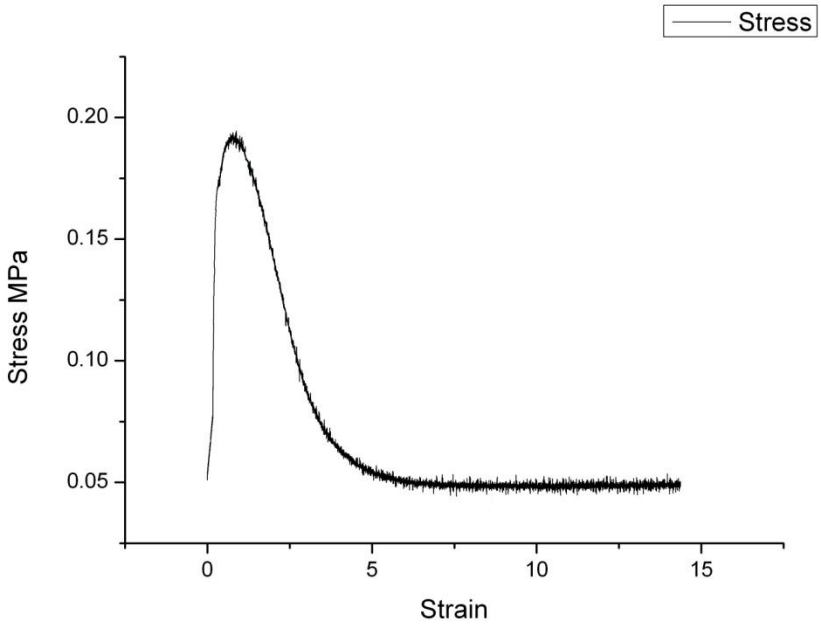


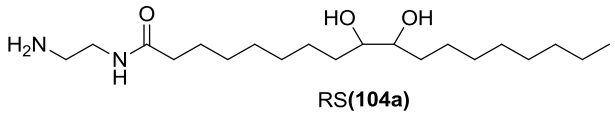
Figure 4.19: Stress strain curve for PU RS**(102) with PEG400**

As shown in Table 4.5 you can see that the addition of the PEG 400 causes the Young's modulus to drop significantly to give a figure of 5.13 MPa. The lower the value you obtain for this, the less stiff the sample. This sample was extremely stretchy, with an approximately 125 % increase in length before failure; however the PU was not very strong. You can also note that the cross-linking density for this PU is smaller than that found for the samples with higher tensile strength. This lower cross-linking could account for the higher elongation and lower tensile strength. The highest Young's modulus attained was for CB**(102)/**PEG3350 having a modulus of 115.4 MPa. This suggests a stiffer PU; however it was quite brittle, although flexible. However the sample snapped extremely quickly with a <1 % increase in length.

When the ratio of biodiol to PEG was increased you found that the stiffness of the polyurethanes were greatly reduced, with the tensile strength dropping from 115.4 to 40.3 MPa and 52.7 to 30.5 MPa respectively.

4.5. Polyurea/Polyurethanes from Vegetable Oils

A second type of polyol was synthesised, one that contained not only two hydroxyl groups but also a more nucleophilic amine derivative RS**(104a)**. Rapeseed oil was reacted with ethylenediamine, without solvent as in section 2.4.1 to give a fatty amide. The unsaturation was then removed *via* epoxidation using mCPBA in chloroform, followed by ring opening of the epoxide using orthophosphoric acid at 100 °C to give a diol RS**(104a)** (Figure 4.20), or in some cases a polyol due to the differing amounts of unsaturation found in the fatty acid chains of rapeseed oil.



RS**(104a)**

Figure 4.20: Example of a diol made from a dihydroxylated fatty amide

On reaction of this polyol RS**(104a)** with (5.59 g) of MDI in a one to one mole ratio with 100 mL of chloroform we found that gelation occurred almost instantly upon heating the mixture indicating rapid reaction and potential cross-linking of the material. This was to be expected as there are at least three nucleophilic components to the polyol. It is known that changing the temperature and concentration of polymerisation can affect the rates of cross-linking reactions. Carrying the reaction out in a less concentrated solution allowed polymeric material with less cross-linking

to be isolated and tests carried out. Terminal amines are often reacted with diisocyanates resulting in polyureas (Figure 4.21). An example of where polyurethanes and polyureas are copolymerised is in spandex, the strong, elastic polymer often used in clothing.[202]

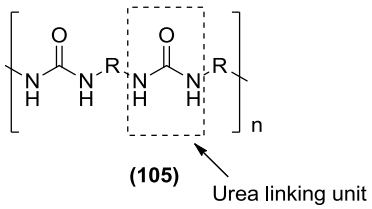


Figure 4.21: Generic polyurea where R can be an aromatic or aliphatic portion of diisocyanate.

Further polyurethanes were prepared from polyol RS**(104a)** and MDI using the three commercially available polyols (PEG 400, PEG 3350 and butanediol) in the same way as with the diethanolamine derived polyols (CB**(30)**/CB**102,** RS**(30)**/RS(**102)**) investigated previously. The thermal and swelling properties were then investigated and compared with the diethanolamine polyurethane set.

PEG/BD	**Physical properties**	Pull apart by hand?
N/A	Soft elastic solid	Yes
BD	Hard brittle solid	Yes
PEG400	Soft tough solid	No
PEG3350	Hard tough solid	No

Table 4.6: Physical properties and strength of RS(104a) derived PU's

PEG/BD	Cross-link density (mol/cm^3) $x10^{-4}$	Swell % (water)
N/A	297.9	3.6
BD	163.7	5.3
PEG400	104.3	7.4
PEG3350	95.3	

Table 4.7: Swelling and cross-link results of polyurethanes derived from RS(104a).

Mechanical testing was unable to be carried out due to failure to produce suitable 'dog-bone' samples, as obvious shrinkage was observed during curing. Shrinkage is often found in thermoset polyurethanes, mainly when materials have high exotherms. Although not measured it is likely the large number of polymerisable groups on the polyol (as well as the more nucleophilic amine group) would be responsible for this. The samples however were extremely tough, and relatively resilient towards solvent and water. A general trend was seen with the swelling results. With the higher MWT commercial diols used you found that more swelling occurred in both water and toluene. DSC of these PU samples also yielded no Tg or melt/softening points. Cross-linking density was calculated however, and are shown in Table 4.7. In comparison to those calculated for the PU samples derived from RS**(102)**, CB**(102)**, RS**(30)**, CB**(30)** the densities for RS**(104a)** are much higher which is likely to be caused by the terminal amine group and extra alcohol groups found in the side-chains of rapeseed derivatives (Figure 4.20) that is found in this polyol. It can also be noted that the cross-linking density decreases as longer chain diols (e.g. PEG 3350) are introduced. This may be due to the components capable of cross-linking being separated by longer chain diols.

4.6. Summary and Conclusions

Diols **(30)** can be made from the amidation of triglycerides **(1)** with diethanolamine **(62e)** and sodium methoxide. Further epoxidation can take place at the unsaturation in the fatty chains to yield functionalised diols **(102)**. These diols (CB**(30)**/CB**(102),** RS**(30)**/RS**(102)**) can be used successfully in the preparation of polyurethanes giving solid brittle polyurethanes with a glassy appearance. The addition of commercial polyols (1,4-butanediol, PEG400 and PEG3350) again yield solid PU samples. Significant cross-linking occurred (presumably due to allophanates and biurets) and this was responsible for the brittle materials obtained. Cross-linking was greater for epoxidised monomers **(102)** where further cross-linking can occur *via* ring-opening of the epoxides under the reaction conditions (presumably by nucleophilic hydroxyl functionality). The most flexible material (with 125 % elongation on break) RS**(102)**/PEG400 had the lowest cross-linking density as expected. In general the tensile strength of the PU's produced were lower than those of Campanella *et al* who produced materials from monoglycerides of soybean oil (1.7 – 2.3 MPa), although no cross-linking data is presented to allow direct comparisons

PU samples prepared with 1,4-butanediol became more brittle and fell apart very easily. The addition of PEG 400 and 3350 yielded slightly more elastic samples, however they were still fairly brittle to the touch and could be pulled apart by hand.

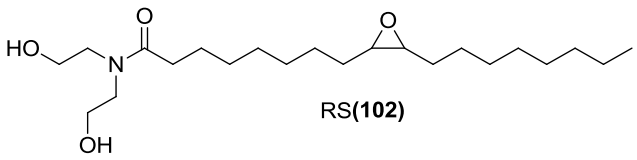
The PU samples prepared from RS**(104a)**, especially when mixed with PEG400 and PEG3350, gave both a hard tough and soft flexible PU respectively. However with the method used in the preparation of these PU samples shrinkage was observed on curing making it difficult to produce good samples for further testing. Cross-linking density for these polyols indicate a higher amount of cross-linking, which would be

attributed to the terminal amine found in this polyol as well as the extra alcohol groups arising from linolenic and linoleic side-chains.

Chapter 5.0 Synthesis of Polyol Oligomers as Potential Monomers for PU Synthesis

5.1. Ring Opening of Epoxides with $BF_3.OEt_2$

As stated earlier, low molecular weight polyols (0.4 – 1.0 KDa) with 3-8 hydroxyl groups are normally used to make rigid polyurethanes, while the larger polyols (2-10 KDa) with less hydroxyl groups (2-3) can be used to make elastomeric materials. In the previous chapter we prepared relatively small molecular weight monomers (~ 350 Da) with 2 hydroxyl groups and the materials produced were generally brittle and not useful. In order to prepare more useful elastomeric PU's we decided to investigate the ring-opening polymerisation of our amidated epoxide vegetable oil derivatives RS**(102)**/CB**(102)** to give larger polyols (2-5KDa) with 2-3 hydroxyl groups. We chose epoxidised cocoa butter and rapeseed oil as feedstocks as they would contain minimal amounts of monomers with 2-3 epoxide groups.



RS**(102)**

Figure 5.1:Amidated epoxidised vegetable derivatives.

Previous work in the Clark group and others has looked into the preparation of vegetable oil based polyols by taking epoxidised oils and ring-opening with $BF_3.Et_2O$ and alcohols to give oligomers.[203,204] Lligadas *et al* investigated the synthesis of polyurethanes from epoxy stearic acid methyl ester **(105)** based

polyether polyols. Polyols **(107)** were prepared by the ring-opening of **(105)** using $HSbF_6$ at RT for 1 h, followed by reduction with $LiAlH_4$ in THF, (Figure 5.2).[205] Polyurethanes were subsequently prepared using MDI that could behave as either rigid plastics or hard rubbers.

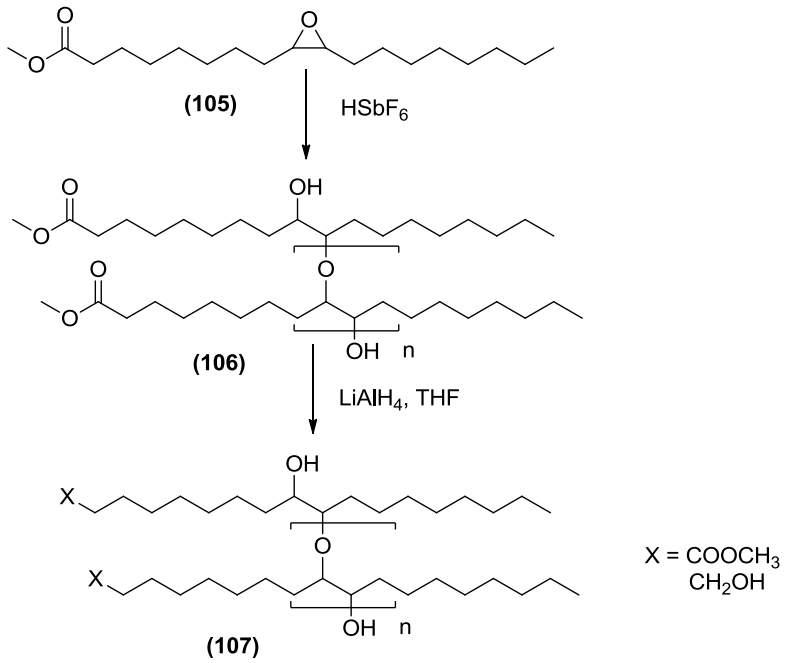


Figure 5.2: Preparation of oligomers from 105 for use in PU synthesis

Recent work in the group[204] has shown that by using this technique PU properties can be altered and flexible elastomers can be produced, especially when palm and euphorbia oil based oligomers were mixed with PEG 3350. As a consequence we decided to investigate the oligomerisation of amidated epoxides **(102)** from both cocoa butter and rapeseed oil, (Figure 5.1).

5.2. Initial Reactions and GPC Characterisation of Oligomers.

Initial investigations involved reaction of either CB**(102)** and RS**(102)** with 0.5 equivalents of $BF_3.Et_2O$ in DCM under nitrogen at reflux for 24 h. The idea was that the hydroxyl groups would initiate a ring-opening of an epoxide in another molecule of **(102)** giving rise to an oligomerisation **(108)**.

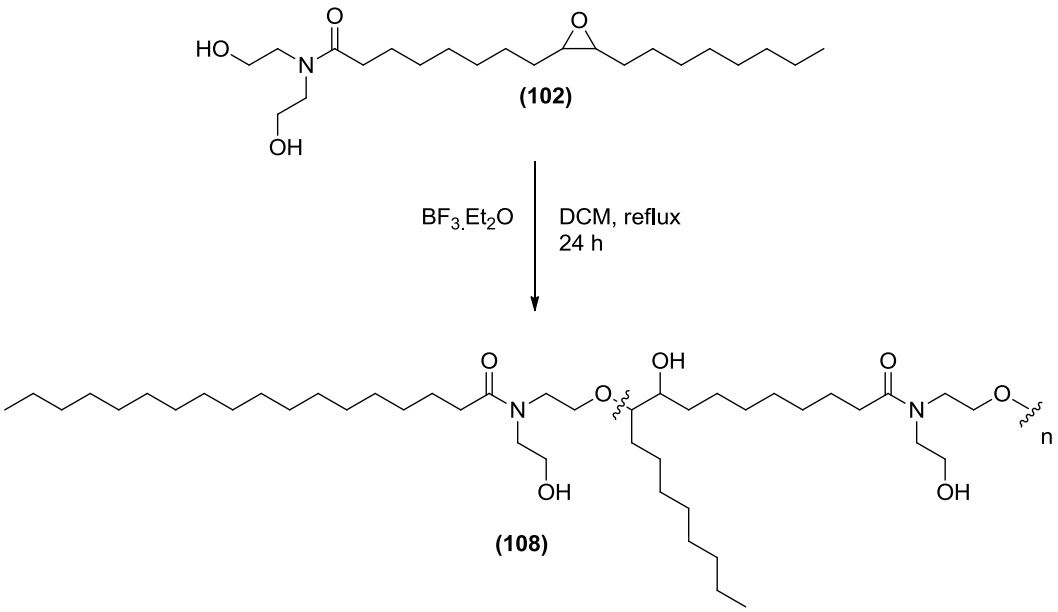


Figure 5.3: Reaction of (102) with $BF_3.Et_2O$

Figure 5.4 showing an example of a possible ring-opened dimer **(108)** after reaction with $BF_3.Et_2O$.

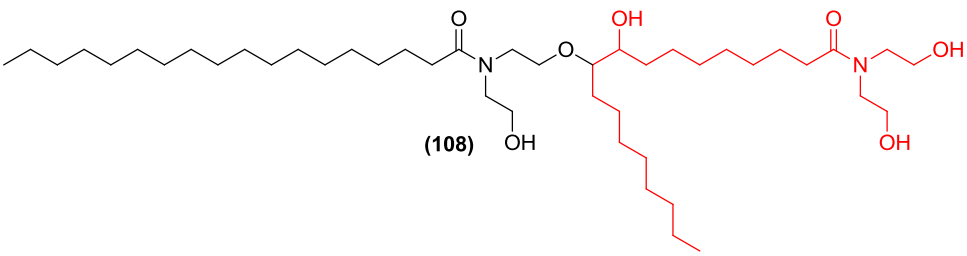


Figure 5.4: Possible ring opening of epoxide (102) using $BF_3.Et_2O$ with hydroxyl from a second fatty amide (102) to yield (108).

Analysis of both the monomer CB**(102)** and the crude oligomerisation mixture CB**(108)** indicated that oligomerisation had partially occurred. Even though the GPC column was not calibrated for this type of polymer (instead calibrated for MMA), by running the monomer itself first (and obtaining a Mn of 608) we were confident that dimerisation and trimerisation had taken place.

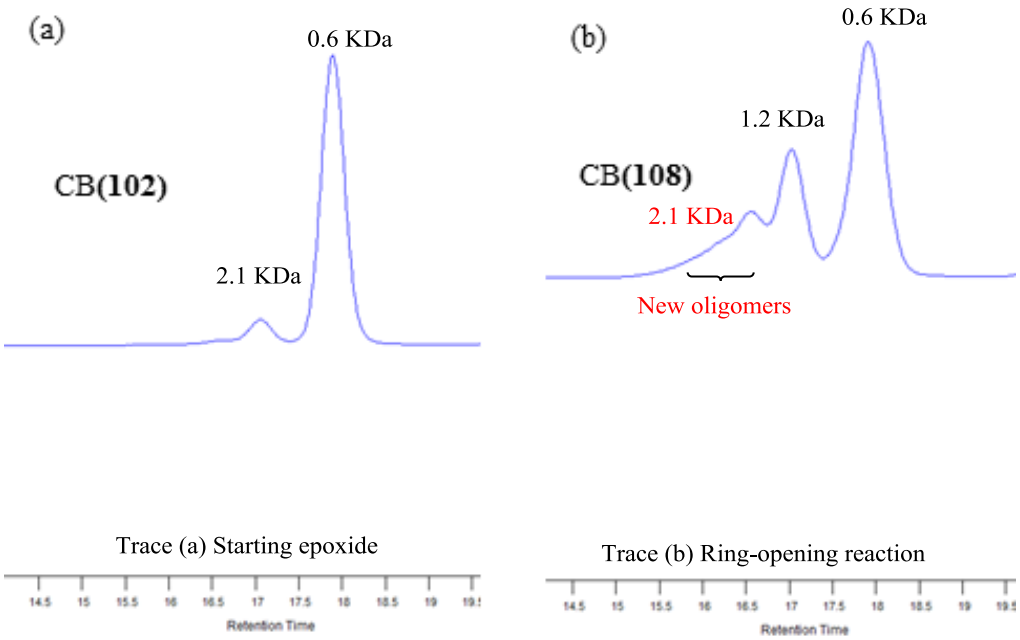


Figure 5.5: (a) GPC trace showing CB(102), (b) GPC trace showing CB(108)

Peak	Mn/KDa	Mw/KDa	PDI	% Area
1	1.2	1.2	1.02	9.0
2	0.6	0.6	1.02	90.9

Table 5.1: Molecular weights from trace (a), (Figure 5.5)

Peak	Mn/KDa	Mw/KDa	PDI	% Area
1	2.1	2.2	1.05	21.3
2	1.2	1.2	1.02	24.7
3	0.6	0.6	1.03	54.0

Table 5.2: Molecular weights from trace (b), (Figure 5.5)

Figure 5.5, trace (a) shows the starting epoxidised cocoa butter monomer CB**(102)** by GPC. There are two peaks; the molecular weights reported in Table 5.1 suggests that the largest peak corresponds to the single epoxidised diol CB**(102)**. The second

smaller peak has a molecular weight roughly double the first one suggesting some form of dimer is already incorporated into the starting mixture. The GPC trace for the $BF_3.Et_2O$ ring-opened product, (Figure 5.5, trace (b)) shows 3 peaks. The original peak corresponding to the monomer, an increase in the second peak corresponding to a dimer and a third peak with a molecular weight (Table 5.2) roughly 3 times that of the monomer peak suggesting a trimer, potentially formed by the desired ring-opening of the epoxide. ^{1}H NMR 400MHz results seem to corroborate this hypothesis (Figure 5.6) as the epoxide proton peaks usually seen at ~2.90 ppm have disappeared. It can also be observed that the shifts at ~3.50 and 3.70 ppm corresponding to the diethanolamine CH_2 protons have begun to shift; suggesting that the OH protons play some role in the reaction as predicted.

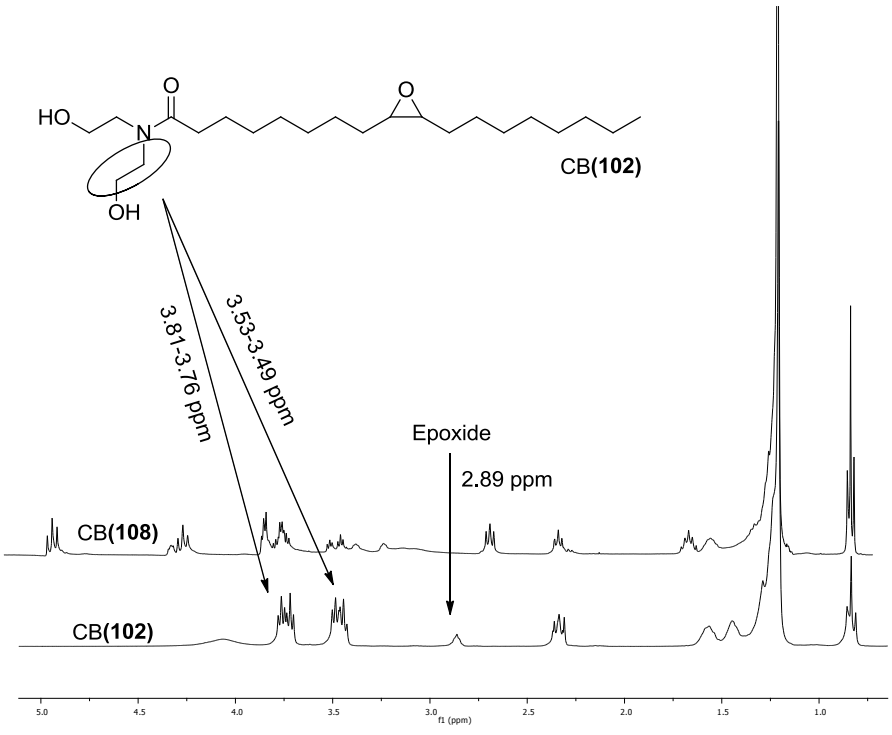
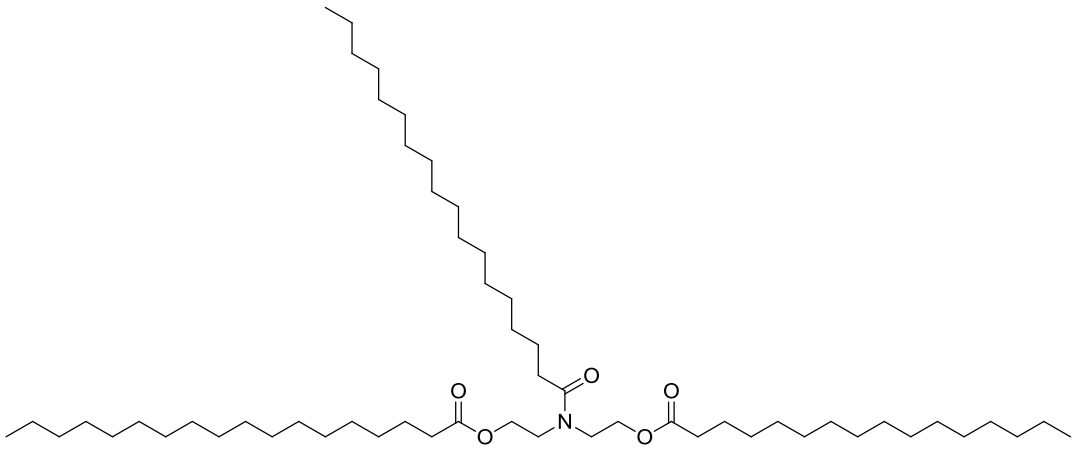


Figure 5.6: 400MHz ^{1}H NMR spectra showing CB(102) (bottom) and CB(108)

However, we also see the appearance of a new triplet at ~4.85ppm which suggests an ester linkage, similar to the peaks found between 4.33 and 4.11 ppm in triglycerides

This suggests that the dimerization and trimerization may also be caused by transesterification of the free hydroxyl groups to give a structure resembling those in Figure 5.7.



(109)

Figure 5.7: Example of transesterified fatty amide

The rapeseed based amide RS**(102)** was reacted in the same way under the same conditions and GPC (Figure 5.9) shows that both the starting material and products molecular weight distribution seemed similar. The GPC traces for the starting RS**(102)** (Figure 5.9 trace (a)) however does show more than one peak. The largest peak has a molecular weight of approximately that of one diol. However it also contains two smaller peaks that have molecular weights of approximately double and triple that of the single diol. This suggests as with the cocoa butter analogue that the starting material was a mixture of oligomers.

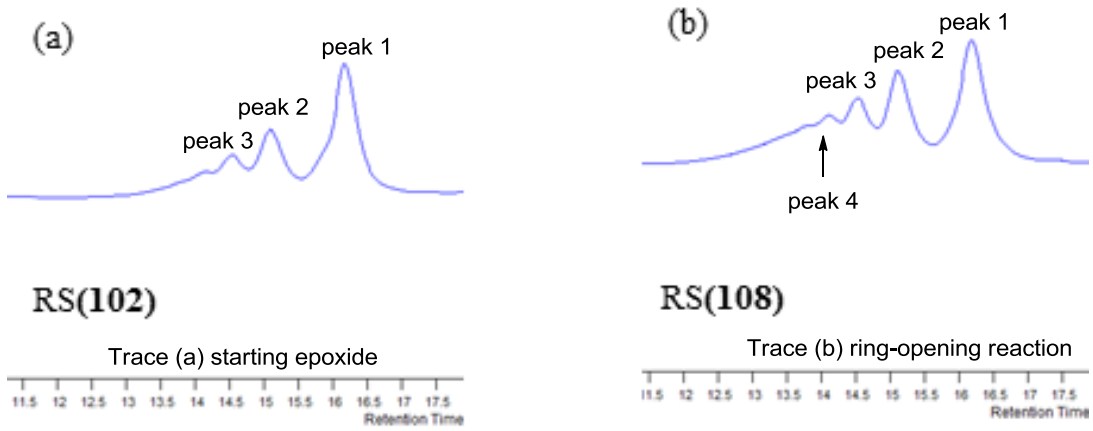


Figure 5.9: (a) GPC trace showing RS(102), (b) GPC trace showing RS(108)

Peak	Mn/KDa	Mw/KDa	PDI	% Area
1	1.9	2.1	1.06	16.5
2	1.2	1.2	1.01	26.9
3	0.6	0.6	1.02	61.1

Table 5.3: Molecular weights from trace (a), (Figure 5.9)

Peak	Mn/KDa	Mw/KDa	PDI	% Area
1	2.9	3.2	1.11	26.2
2	1.7	1.7	1.01	16.0
3	1.2	1.2	1.01	22.3
4	0.6	0.6	1.03	35.5

Table 5.4: Molecular weights from trace (b), (Figure 5.9)

The GPC trace (Figure 5.9 (b)) of RS**(102)** on reaction with $BF_3.Et_2O$ as with the cocoa butter analogue CB**(102)** suggests that some oligomerisation is taking place; 4 peaks are shown with molecular weights corresponding to approximately 1, 2, 3 and 4 monomer units with a slight increase in intensity of the second largest peak.

^{1}H NMR data also indicated that ring opening of the epoxide was taking place due to the reduction of the integral of the epoxide proton peaks (Figure 5.10). However it is apparent that unlike cocoa butter, with 0.5 equivalents of $BF_3.Et_2O$ not all of the epoxides reacted. This is likely due to the increase amount of unsaturation found in

rapeseed oil in comparison with cocoa butter, and subsequently increased number of epoxides.

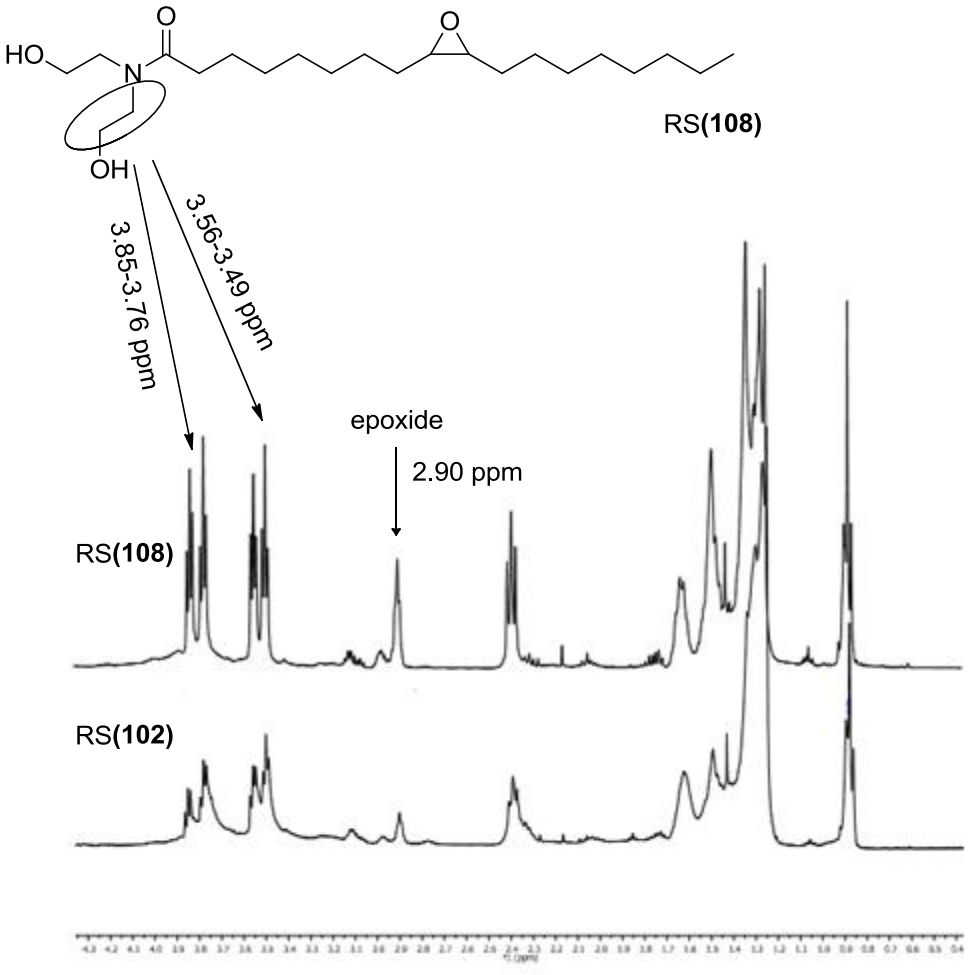


Figure 5.10: 400MHz ^{1}H NMR spectra showing RS(108) before and after reaction with $BF_3.Et_2O$ (RS(102))

Broadening of the peaks corresponding to the diethanolamine CH_2 protons also occurred as before but we did not see the appearance of any peaks at 5.00 to 4.00 ppm range suggesting that no transesterification is taking place as for the CB**(108)**. Other evidence for this differential reactivity was found in the infrared spectra of both CB**(108)** and RS**(108)**. The IR for this rapeseed based oligomer RS**(108)** showed only one C=O peak at 1629 cm^{-1} characteristic of the amide functionality,

while the cocoa butter derivative CB**(108)** showed two C=O absorbance peaks with the second at 1734 cm^{-1} characteristic of an ester.

5.3. Alternative Approach.

The fact that the starting amides CB**(102)** and RS**(102)** themselves showed evidence of oligomerisation is probably a consequence of their preparation. The epoxidised monomers had been synthesised by first epoxidising the starting triglycerides **(1)**, rapeseed oil and cocoa butter using the tungsten based catalyst and H_2O_2 method (Figure 5.11) described in section 2.3; these were then further reacted with diethanolamine **(62e)** using the conditions reported in section 2.4.1.

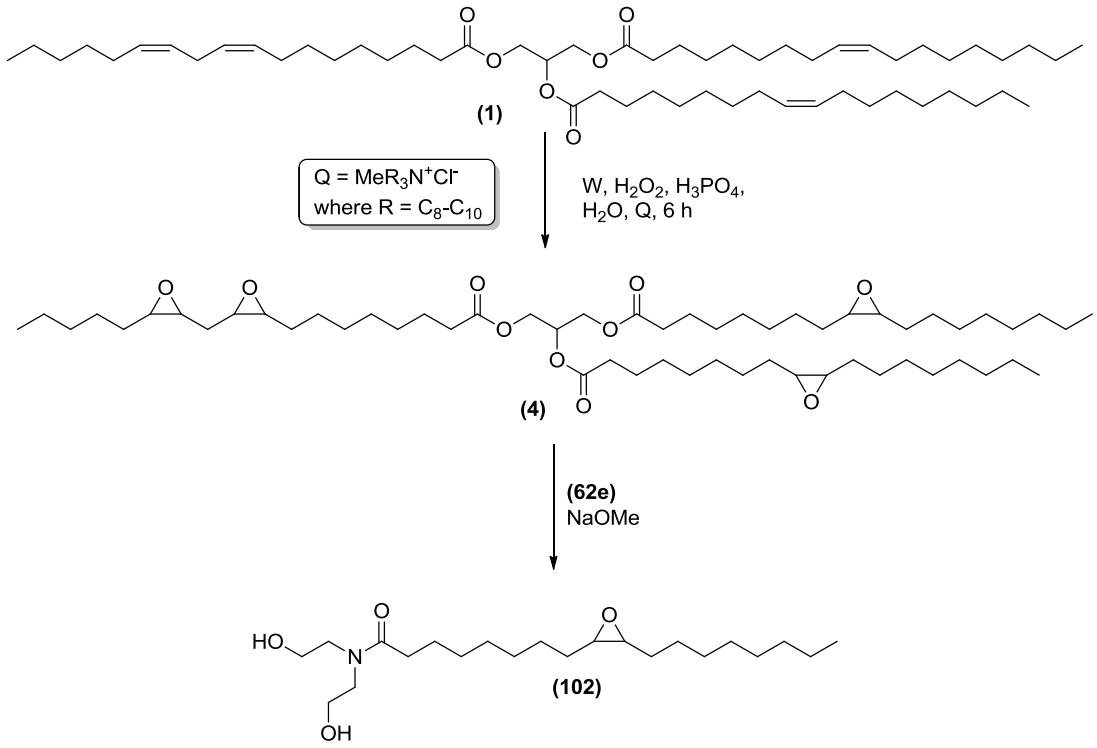


Figure 5.11: Epoxidation of triglyceride with W cat.

One drawback of synthesising the monomers in this order is that of competition between nucleophilic transesterification (attack at ester) or epoxide ring-opening of **(4)**. This means that the starting amide RS**(102)** and CB**(102)** could contain ring-opened products **(110)** before the addition of $BF_3.Et_2O$. That this was possible was reported by Lee *et al* when attempting to react epoxidised palm oil with diethanolamine (Figure 5.12).[195]

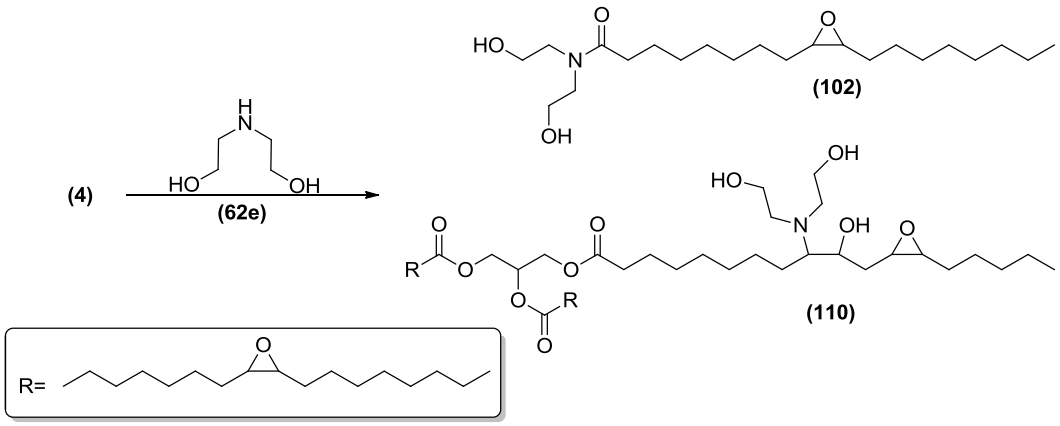


Figure 5.12: Reaction of diethanolamine (62e) with epoxidised vegetable oil (4)

Consequently, we re-synthesised the two starting amides RS**(102),** CB**(102)** by reversing the order of the reactions (Figure 5.13).

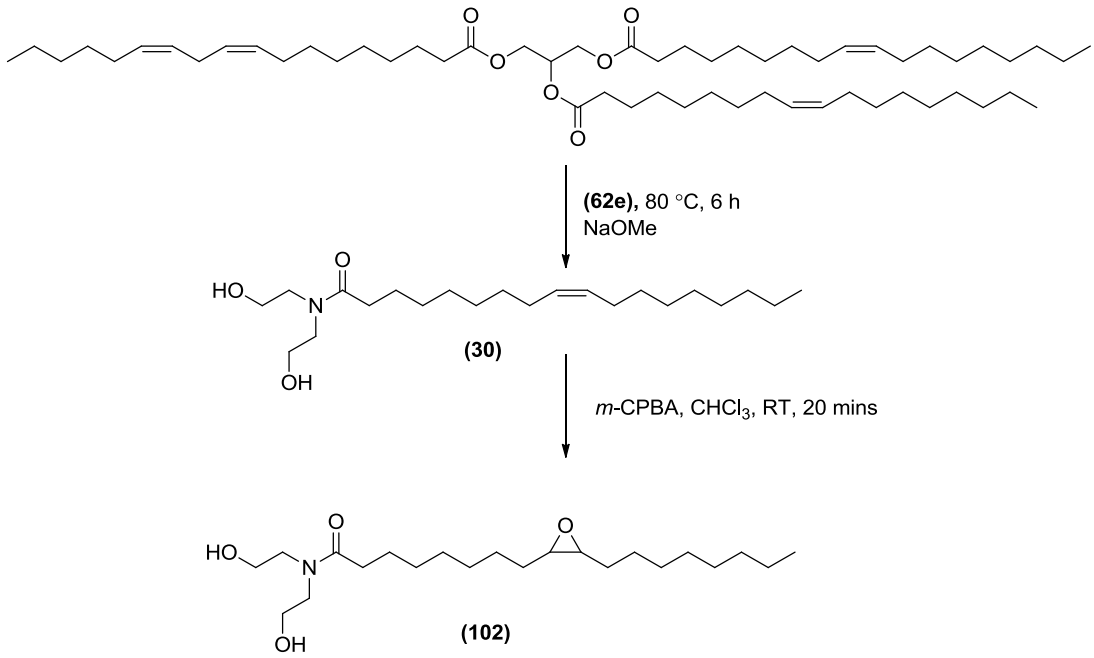


Figure 5.13: Triglyceride undergoing aminolysis with diethanolamine (62e) followed by epoxidation

Hence reaction of the **(1)** with **(62e)** using the procedure described in section 2.4.1 produced the desired fatty amides **(30)** which were then epoxidised using mCPBA to give CB**(102)** and RS**(102)**. Figure 5.14 shows the GPC traces for the cocoa butter and rapeseed analogues synthesised *via* this method.

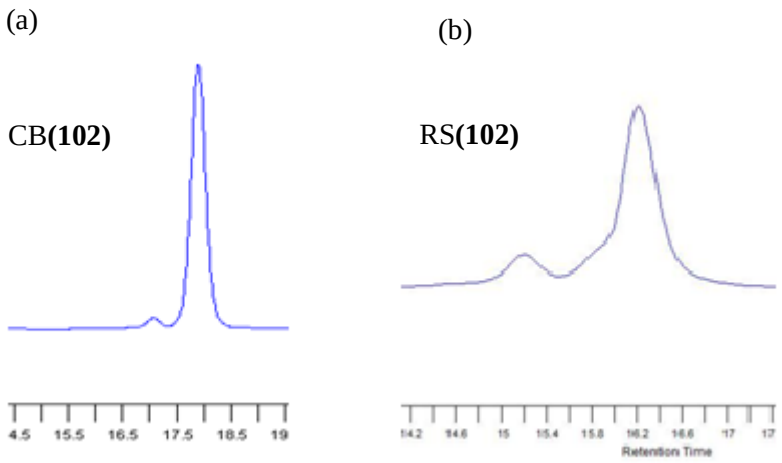


Figure 5.14: (a) GPC trace showing CB(102), (b) GPC trace showing RS(102) both synthesised *via* route 2.

Analysis indicates that while the cocoa butter monomer has a similar molecular weight profile, irrespective of its synthetic route, the rapeseed monomer is different for both routes. The second approach provides a much 'cleaner' monomer with less high molecular weight material. Oligomerisation of both sets of monomers was carried out as before and both clearly undergo an oligomerisation process.

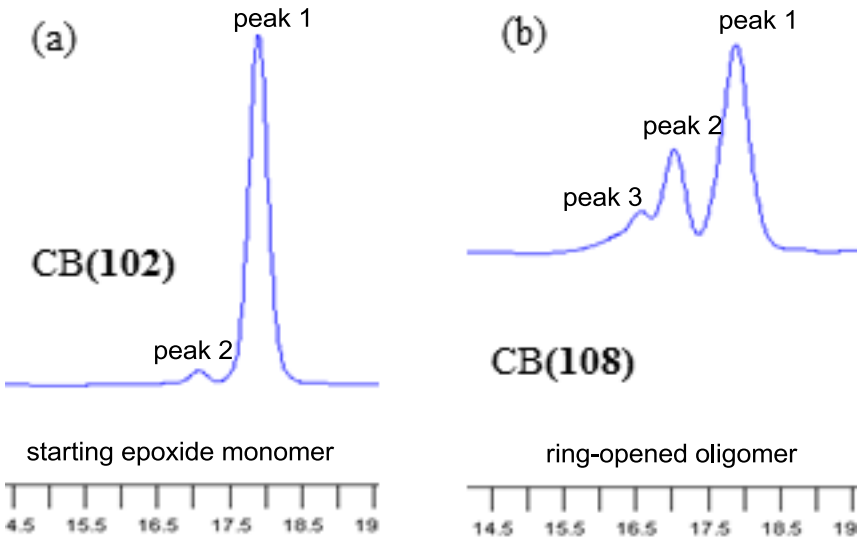


Figure 5.15: GPC traces showing (a) CB(102) , (b) CB(108) synthesised *via* route 2

Peak	Mn/KDa	Mw/KDa	PDI	% Area
1	1.1	1.1	1.03	0.9
2	0.5	0.5	1.01	88.2

Table 5.5: Molecular weights from trace (a), (Figure 5.15)

Peak	Mn/KDa	Mw/KDa	PDI	% Area
1	1.9	2.1	1.08	12.7
2	1.1	1.1	1.02	24.4
3	0.5	0.5	1.03	62.9

Table 5.6: Molecular weights from trace (b), (Figure 5.15)

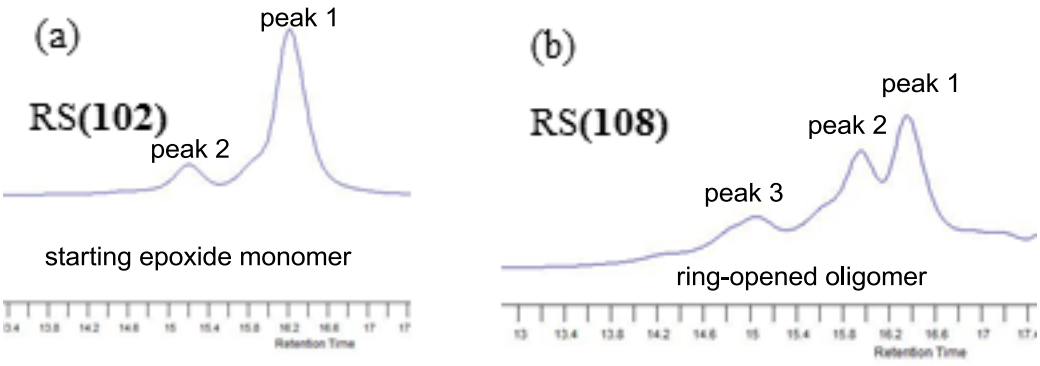


Figure 5.16: GPC traces showing (a) RS(102) , (b) RS(108) synthesised *via* route 2

Peak	Mn/KDa	Mw/KDa	PDI	% Area
1	1.2	1.2	1.05	2.5
2	0.5	0.5	1.06	97.5

Table 5.7: Molecular weights from trace (a), (Figure 5.16)

Peak	Mn/KDa	Mw/KDa	PDI	% Area
1	2.1	2.2	1.12	29.7
2	1.2	1.3	1.03	32.8
3	0.5	0.6	1.07	37.5

Table 5.8: Molecular weights from trace (b), (Figure 5.16)

5.4: Summary and Conclusions

Oligomeric polyols can be prepared *via* two different routes. Epoxidised triglyceride **(4)** can undergo aminolysis to yield the amide derivative **(102)**, or raw triglyceride **(1)** can undergo aminolysis followed by epoxidation. Oligomerisation **(108)** is then afforded using $BF_3.Et_2O$ in DCM. The two different routes can yield different polyols depending on the triglyceride. With cocoa butter (CB**(1)**) a similar product **(102)** is yielded with both methods; when rapeseed oil (RS**(1)**) is used however there is significant amount of oligomer **(108)** observed prior to the oligomerisation step when starting with epoxidised rapeseed oil. This could be attributed to the epoxides

undergoing ring-opening during the aminolysis step as significantly more epoxides is observed in rapeseed oil in comparison to cocoa butter. On reaction with $BF_3.Et_2O$ with both sets of polyol oligomerisation **(108)** can be observed.

Future work will focus on the use of these *oligomeric* macromonomers in PU synthesis and comparison of the properties of these novel materials with those prepared from the '*monomeric'* monomers described in section 4.2.

6.0 Conclusion and future work

A selection of amide monomers were successfully prepared from various vegetable oils and fats with different degrees of unsaturation, and five different amines, **(62a-e)**, including amino alcohols **(62d-e)** and diamines **(62a-c)** (Figure 6.1).

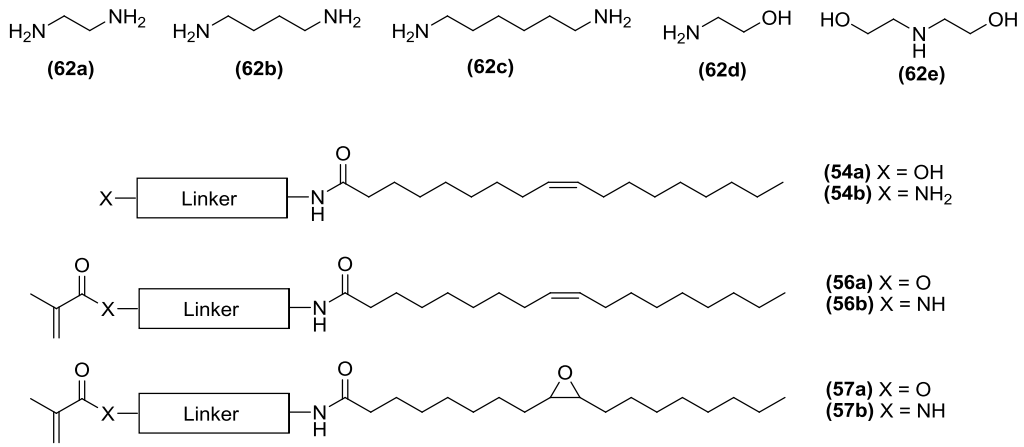


Figure 6.1: Ethanolamines and diamines used in aminolysis reactions, and subsequent amides and monomers synthesised using these linkers.

These amides were initially synthesised for the purpose of incorporation into polymer latexes for potential use in paint binders. Methacrylate functionality was incorporated using methacryloyl chloride, to allow for polymerisation. Both the amides and monomers were synthesised in good yields (71 – 93 %). The amides and monomers derived from the ethanolamines, gave products as viscous oils, whereas the diamines gave waxy solids, which is probably due to increased H-bonding. Yellowing has always been a problem with paints derived from oils, partially due to the unsaturation in the chains. Removal of these double bonds was therefore carried out *via* epoxidation, to investigate whether this could decrease the amount of

yellowing seen in the finished latex films. Epoxidised monomers were synthesised using mCPBA with yields of 58 - 89 %. The cocoa butter monomers were found to give the lowest yields, possibly due to difficulty in dissolving the monomers.

It was found that these methacryloylated amides, both unsaturated and epoxidised, were generally capable of polymerising in water based systems. However, monomers with increased saturation (cocoa butter) and epoxides, became more difficult to incorporate into emulsion, which was due to these monomers being unable to fully dissolve in the solvents used in the procedures. Of the monomers successfully incorporated, clear cohesive final films were observed, with the epoxidised monomers imparting more flexibility to the films, possibly due to plasticiser quality of epoxidised oils The flexibility and hardness of the films were measured using a Sheen pendulum hardness rocker. Additional tests on the final films, included GPC, MFFT and Tg. Due to the high gel content and the difficulty in fully dissolving the latexes in appropriate solvents, the GPC results were unreliable. MFFT results gave temperatures in the range of 7 - 12 °C. These results are promising with regards to interior decorative paints, as ideal MFFTs for these are usually between 7 °C and 10 °C, approximately 10 °C lower than room temperature. Tg results for the latexes were extremely low, ranging from -47 - -55 °C. This is unusual given that 90 % of the monomers used in the formulations were BMA, which has a Tg between 21 °C and 28 °C, and therefore a higher Tg, closer to that of BMA, would be expected for the latexes.. It is possible that only the biomonomer Tg was observed, as when thermal analysis of a pBMA latex was investigated, it was difficult to discern a Tg with the ramping rate used. With more time, a slower ramping rate could be used to see if a higher Tg is observed.

Decreased yellowing was observed in the films when epoxidised monomers were used. However, the use of cocoa butter derived monomers gave the opposite effect, actually increasing the amount of yellowing with respect to the unsaturated samples. Using the yellowing scale in Chapter 3 (Figure 3.7), the degree of yellowing seen in the cocoa butter and unsaturated latexes reached 7 and 6 respectively, whereas the partially epoxidised sample only reached 2. Unsaturation can therefore only be a part of the reasoning behind yellowing.

Due to slight blooming observed on some of the dry latex films, it was suggested that the biomonomer may not be copolymerising with the BMA used in the formulation, and instead giving a mixture of homopolymers. AFM images indicated two different phases which seemed to support this. Further investigation would be needed, potentially using electron microscopy or by centrifugation, to see if separation of polymers could be achieved and subsequently analysed. It would be interesting to follow the progression of polymerisation over time, to see whether co-polymerisation is taking place. Having homopolymers instead of copolymers could also be contributing to the yellowing seen in the latexes.

Increasing the percentage of biomonomer used in the latex formulations (to 15 and 20 wt%) was briefly investigated. Preliminary results showed incorporation into a polymer latex could be achieved, however, it was still uncertain as to whether copolymers were being produced. Softer latex films were formed with a lower MFFT and increased yellowing was observed both before and after heating. The production of softer latexes was due to the increase in soft monomer (biomonomer) being used in the formulation. The incorporation of biomonomers into the latexes

also showed an increase in gel content to 35 and 40 % when compared to BMA control, and 10 % biomonomer incorporation which gave 0 and 30 % respectively.

A small selection of monomers were also successfully synthesised in a one step process, using HEMA (RS**(80)**), allylamine (RS**(77b)**), and allyl alcohol (RS**(77a)**) in good yields.

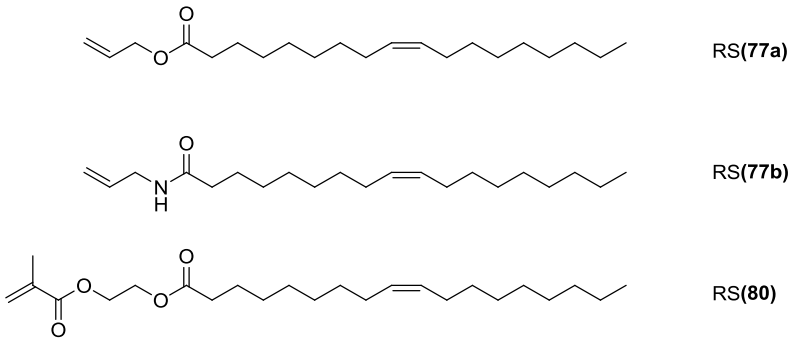


Figure 6.2: Monomers synthesised in one step from rapeseed oil as allylamine, allyl alcohol and HEMA.

With more time, scale up of these monomers could be achieved to allow for testing in latex systems. The HEMA monomers would be expected to react in a similar way to the methacryloyl monomers, due to similar functional groups, however, the allyl alcohol and allylamine based monomers would most likely react differently. Allyl monomers are not widely known to readily form homopolymers *via* radical polymerisation. This could mean that under current conditions, these would be more likely to form the desired copolymers or not polymerise.

The amides produced using diethanolamine **(62e)**, were subsequently used as diols (both epoxidised **(102)** and unsaturated **(30)**) (Figure 6.3) with MDI in the synthesis of polyurethanes.

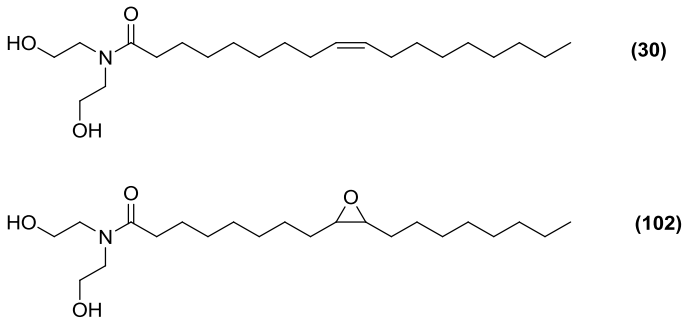


Figure 6.3: Epoxidised and unsaturated diols synthesised from triglyceride and diethanolamine (62e)

Successful plastics were produced both with and without the aid of commercial diols (PEGs and 1,4-butanediol). The majority of plastics produced were however, extremely glassy and brittle, making tensile testing difficult. The production of such brittle samples was unexpected, as it suggested a highly cross-linked network, which is unusual as only diols were used. This could mean that allophanates or biurets were forming. Given more time this could be investigated further, by potentially using lower temperatures and ensuring isocyanate content was at a minimum. When epoxidised diols were used, further cross-linking was observed, suggesting that the epoxides could also be a cause of cross-linking. The cross-linking density was measured using the Flory-Rehner equation, which utilises the polymer density and the swelling ratio. IR could potentially be used as a means of testing whether allophanates or biurets were being formed, by observing the carbonyl region, as the formation of these would introduce a second carbonyl environment.

Finally, these epoxidised diols were reacted with $BF_3.Et_2O$ to encourage ring opening and oligomerisation to give larger polyols, for potential use in the synthesis of polyurethanes. Future work would involve a more thorough analysis of these oligomeric products and an investigation into whether they could be successfully incorporated into polyurethanes. A comparison with those prepared using just the original diols could then be made. Due to previous work in the Clark group, it is postulated that these larger oligomeric polyols would form more flexible, less brittle polyurethane products.

7.0 Experimental

7.1 General Procedures and Information

The starting materials used in the syntheses were obtained from commercial suppliers and used as bought. Heat transfer was achieved using drysyn© apparatus for synthesis of monomers, oil bath in standard polymerisations and heated water jacket for emulsion polymerisations.

^{1}H and ^{13}C NMR were performed on a Bruker DPX-400 spectrometer, at 400MHz and 100MHz respectively. All chemical shifts were expressed in parts per million (ppm) relative to the internal standard tetrametylsilane (TMS) (0.00ppm), coupling constants (*J*) were expressed in Hertz (Hz). Infrared spectra were recorded on a Perkin-Elmer Avatar 320 Fourier transform spectrometer. Absorption was recorded in wavenumbers (cm^{-1}).

Melting points were measured with a Sanyo Gallenkamp heater, or Metler Toledo DSC1-Star.

TLC was carried out using Merk silica gel coated aluminium sheets as the stationary phase (Merck Kieselgel $60F_{254}$ 230-400 mesh). The tlc plate was visualised under a UV lamp (254 nm) then stained using potassium permanganate solution. The flash chromatography was carried out using Merck 9385 Keisel 60 SiO_2 (230-400 mesh).

Mass spectrometry was achieved using electrospray ionisation. Low resolution was performed on a Bruker Esquire 200 machine, an accurate mass spectrometry was

available through the in house mass spectrometry service on a Bruker HCT or HCT ultra machines.

GPC with THF as the eluent was performed on an Agilent 390-MDS with an autosampler and a PLgel 5.0 µm bead-size guard column (50 x 7.5 mm), followed by two linear 5.0 µm bead-size PLgel Mixed D columns (300 x 7.5 mm) and differential refractive index detector. The GPC system was calibrated using linear poly(methyl methacrylate) EasiVial standards (Agilent Ltd.) range from 200 to 10^5 Da. Data was collected and analysed using Cirrus GPC/SEC software (version 3.3).

Fatty acid composition by gas chromatography was carried out by Warwick HRI.

The following compounds were synthesised using oils and so contain mixtures. The names of each compound pertain to the structure drawn however the analysis reflects a number of products. For unsaturated products cocoa butter derived products are denoted with stearic chains, rapeseed with oleic chains and soybean with linoleic chains.

7.2 General Procedures for Reactions Performed in Chapter 2

7.2.1 General Procedure for the Synthesis of Fatty Acid Amides.

Amine (4.5 equiv.) and triglyceride (1 equiv.) were heated to between 80 and 110 °C with sodium methoxide under a nitrogen atmosphere for 6 hours. Reaction was allowed to cool to room temperature and crude product dissolved in organic solvent, washed with 15% $NaCl_{(aq)}$, dried over Na_2SO_4, filtered and evaporated in *vacuo* to

produce product, no further purification required for diethanolamine substrates, diamine substrates were filtered through a silica plug.

7.2.2 General Procedure the Synthesis of Methacryloylation of Amides

Triglyceride amide (1 equiv.) dissolved in DCM followed by addition of triethylamine (1 equiv.). Reaction mixture cooled to 0°C in an ice bath. Methacryloyl chloride (1 equiv.) added dropwise over 1 h under a nitrogen atmosphere. The reaction was allowed to reach room temperature overnight. Crude reaction mixture was washed with $NaHCO_3$ (aq), dried over Na_2SO_4 and concentrated in *vacuo* to give product, no further purification was undertaken.

7.2.3 General Procedure for the Synthesis of Fully Epoxidised Monomers

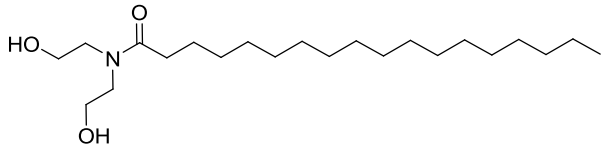
Methacrylated triglyceride amide (1 equiv.) dissolved in $CHCl_3$. mCPBA (2 equiv. for Soybean oil, 1.5 equiv. Rapeseed oil, 0.4 equiv. for Cocoa Butter) added and stirred for 20 minutes at room temperature. Crude product washed with $Na_2S_2O_5$ (4x 250 mL) and $NaHCO_3$ (5 x 250 mL), dried over Na_2SO_4, filtered and dried in *vacuo* to produce product, with no further purification required.

7.2.4 General Procedure for the Synthesis of Partially Epoxidised Monomers

Methacrylated triglyceride amide (1 equiv.) dissolved in $CHCl_3$. mCPBA (1 equiv. for Soybean oil, 0.75 equiv. Rapeseed oil, 0.1 equiv. for Cocoa Butter) added and stirred for 20 minutes at room temperature. Crude product washed with $Na_2S_2O_5$ (4x

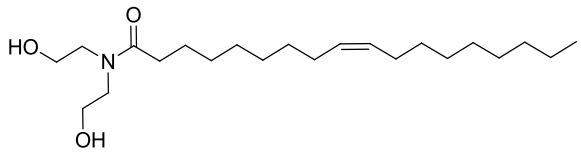
250 mL) and $NaHCO_3$ (5 x 250 mL), dried over Na_2SO_4, filtered and dried in *vacuo* to produce product, with no further purification required.

_N,N_-bis(2-hydroxyethyl)stearamide (CB**(30)) (Synthesised from Cocoa Butter)**



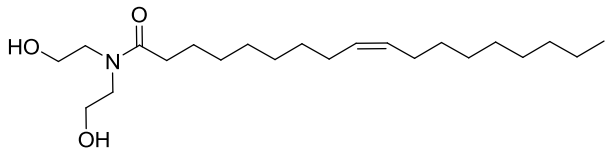
The general procedure for the synthesis of fatty acid amides (7.2.1) was applied using diethanolamine (59.9 g, 0.52 mol), cocoa butter (100 g, 0.11 mol) and sodium methoxide. The reaction mixture was dissolved in diethyl ether (500 mL) and washed with 15% NaCl (aq) (500 mL) to produce CB**(30)** as a creamy orange waxy solid, (103.7g, 82%). m.p. 31-34°C; ν_{max}/cm^{-1} 3395 (O-H broad), 2916, 2848 (C-H), 1619 (C=O amide) 1050 (C-N); δ_H (400MHz, $CDCl_3$): 5.38 – 3.51 (1H, m, HC=CH), 3.80 (2H, t, *J*=5.0, $HOCH_2$), 3.76 (2H, t, *J*=5.0, $HOCH_2$), 3.53 (2H, t, *J*=5.0, NCH_2), 3.49 (2H, t, *J*=5.0, NCH_2), 2.38 (2H, t, *J*=7.5, $O=CCH_2$), 2.07 – 1.97 (2H, m, $=CHCH_2$), 1.67 – 1.55 (2H, m, $O=CCH_2CH_2$), 1.38 – 1.18 (28H, m, CH_2), 0.88 (3H, t, *J*=6.5, CH_3); δ_C (100MHz, $CDCl_3$): 175.84 (C=O), 129.98, 129.74 (HC=CH), 61.26 ($HOCH_2$), 60.71 ($HOCH_2$), 52.27 (CH_2N), 50.51 (CH_2N), 33.60 ($O=CCH_2$), 31.91 ($CH_2CH_2CH_3$), 29.70 - 29.20 (CH_2), 27.21 ($C=CCH_2$), 25.32 ($O=CH_2CH_2$), 22.67 (CH_2CH_3), 14.10 (CH_3); m/z (ES^+) 392.3 $[M+Na]^+$; 394.3 $[M+Na]^+$; 366.3 HRMS (ES+) 392.3229 $[M+Na]^+$, ($C_{22}H_{43}NNaO_3$ required 392.3141); 394.3302 $[M+Na]^+$, ($C_{22}H_{45}NNaO_3$ required 394.3297); 366.3045 $[M+Na]^+$, ($C_{20}H_{41}NNaO_3$ required 366.2984).

***N,N*-bis(2-hydroxyethyl)oleamide (**TO**(30))**



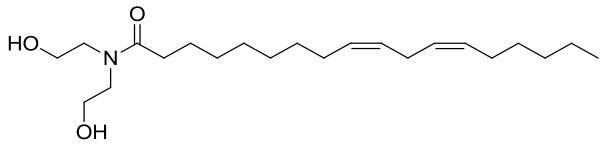
The general procedure for the synthesis of fatty acid amides (7.2.1) was applied using diethanolamine (0.21 g, 2.00×10^{-3} mol), sodium methoxide and glyceryl trioleate (400mg, 4.52×10^{-4} mol) heated to 110 °C. Reaction product dissolved in diethyl ether (10 mL) washed with 15% NaCl (aq) (10 mL) to give TO**(30)** as a viscous orange oil (398 mg, 80%). ν_{max}/cm^{-1} 3367 (OH broad), 2921 (C-H), 1618 (C=O), 1049 (C-N); δ_H (400MHz, $CDCl_3$) 5.40 – 5.28 (2H, m, HC=CH), 4.20 (2H, broad s, OH), 3.81 (2H, t, *J*=5.0, $HOCH_2$), 3.76 (2H, t, *J*=5.0, $HOCH_2$), 3.53 (2H, t, *J*=5.0, H_2CN), 3.49 (2H, t, *J*=5.0, H_2CN), 2.39 (2H, t, *J*=7.5, $COCH_2$), 2.01 (4H, q, *J*=6.5, $=CHCH_2$), 1.66 – 1.57 (2H, m, $O=CCH_2CH_2$), 1.38 – 1.23 (20H, m, CH_2), 0.88 (3H, t, *J*=6.5, CH_3); δ_C (100MHz, $CDCl_3$): 175.68 (C=O), 129.99, 129.75 (HC=CH), 61.39, 60.77 ($HOCH_2$), 52.26, 50.59 (H_2CN), 33.63 ($O=CCH_2$), 31.90 ($CH_2CH_2CH_3$), 29.77 – 29.21 (CH_2), 27.22, 27.21 ($C=CCH_2$), 25.31 ($O=CH_2CH_2$), 22.68 (CH_2CH_3) 14.11 (CH_3); m/z (ES^+) 392.3 $[M+Na]^+$, 370.3 $[M+H]^+$, found: 370.3316 $[M+H]^+$, ($C_{22}H_{44}NO_3$, required 370.3243).

***N,N*-bis(2-hydroxyethyl)oleamide (RS(30)) (Synthesised from rapeseed oil)**



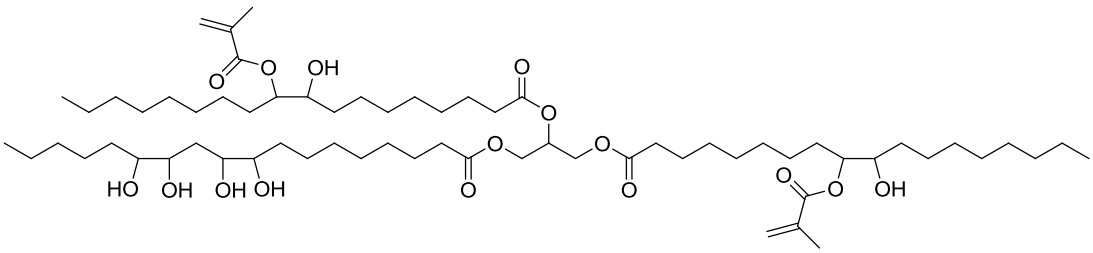
The general procedure for the synthesis of fatty acid amides (7.2.1) was applied using diethanolamine (53.5 g, 48.8 mL, 0.51 mol), sodium methoxide and rapeseed oil (100 g, 0.11 mol) heated to 110°C. Reaction product dissolved in diethyl ether (500 mL), washed with 5% $NaCl_{(aq)}$ (400 mL) to produce RS**(30)** as an orange waxy solid, (89 %). ν_{max}/cm^{-1} 3367 (OH broad), 2921, 2852 (C-H), 1618 (C=O); δ_H (400MHz, $CDCl_3$): 5.45 – 5.24 (3H, m, HC=CH), 3.82 (2H, t, *J*=5.0, $HOCH_2$), 3.77 (2H, t, *J*=5.0, $HOCH_2$), 3.54 (2H, t, *J*=5.0, H_2CN), 3.49 (2H, t, *J*=5.0, H_2CN), 2.84 – 2.73 (1H, m, $CH=CHCH_2CH=CH$), 2.38 (2H, t, *J*=7.5, $COCH_2$), 2.11 – 1.96 (4H, m, $=CHCH_2$), 1.68 – 1.56 (2H, m, $O=CCH_2CH_2$), 1.39 – 1.22 (20H, m, Long chain CH_2), 0.98 (1H, t, *J*=7.5, $=CHCH_2CH_3$), 0.88 (3H, t, *J*=6.5, CH_3); δ_C (100MHz, $CDCl_3$): 175.67 (C=O), 130.21 – 127.11 (HC=CH), 61.32, 60.74 ($HOCH_2$), 52.25, 50.59 (H_2CN), 33.63 ($O=CCH_2$), 31.91 (CH_2) 31.52 (CH_2), 29.75 – 29.22 (CH_2), 27.20 (CH_2), 25.61 (CH_2), 25.30 (CH_2), 22.68 (CH_2), 22.57 (CH_2) 14.12 (CH_3); m/z (ES^+) 392.3 $[M+Na]^+$, 390.3 $[M+Na]^+$, 388.3 $[M+Na]^+$ HRMS (ES+) 392.3239 $[M+Na]^+$, ($C_{22}H_{43}NNaO_3$ required 392.3141); 390.3025 $[M+Na]^+$, ($C_{22}H_{41}NNaO_3$ required 390.2984); 388.2930 $[M+Na]^+$, ($C_{22}H_{39}NNaO_3$ required 388.2828).

(9Z, 12Z)-*N,N*-bis(2-hydroxyethyl)octadeca-9-12-dienamide (SB(30)) (Synthesised from soybean oil)



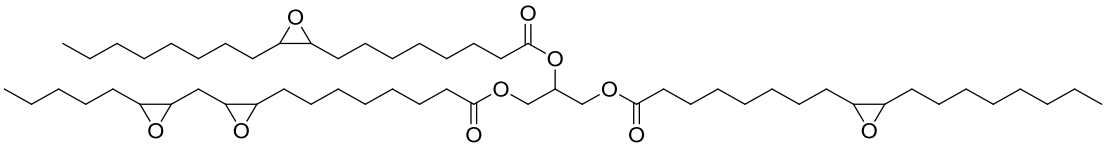
The general procedure for the synthesis of fatty acid amides (7.2.1) was applied using Soybean oil (50g, 0.06 mol), diethanolamine (26.8 g, 0.26 mol,) and sodium methoxide heated to 110°C. The reaction mixture was dissolved in diethyl ether (200 mL) and washed with 15% NaCl (aq) (250 mL) and dried over Na_2SO_4, to give RS**(30)** as a viscous orange oil (59.6 g, 90%). ν_{max}/cm^{-1} 3395 (OH broad), 2916, 2849 (C-H), 1618 (C=O); δ_H (400MHz, $CDCl_3$): 5.46 – 5.26 (3H, m, HC=CH), 4.12 (2H, broad s, $HOCH_2$), 3.81 (2H, t, *J*=5.0, $HOCH_2$), 3.76 (2H, t, *J*=5.0, $HOCH_2$), 3.53 (2H, t, *J*=5.0, H_2CN), 3.49 (2H, t, *J*=5.0, H_2CN), 2.85-2.71 (2H, m, $CH=CHCH_2CH=CH$), 2.38 (2H, t, *J*=7.5, $COCH_2$), 2.10 – 1.98 (4H, m, $=CHCH_2$), 1.68 – 1.54 (2H, m, $O=CCH_2CH_2$), 1.41 – 1.19 (18H, m, side chain CH_2), 0.98 (1H, t, *J*=7.5, $=CHCH_2CH_3$), 0.88 (3H, t, *J*=6.5, CH_3); δ_C (100MHz, $CDCl_3$): 175.67 (C=O), 130.22 – 127.12 (HC=CH), 61.32, 60.75 ($HOCH_2$), 52.27, 50.57 (H_2CN), 33.63 ($O=CCH_2$), 31.90 (CH_2) 31.52 (CH_2), 29.75 – 29.21 (side chain CH_2), 27.20 ($C=CCH_2$), 25.62 ($CH=CHCH_2CH=CH$), 25.30 ($O=CH_2CH_2$), 22.68 (CH_2), 22.57 (CH_2) 14.12 (CH_3); m/z (ES^+) 392.3 $[M+Na]^+$, 390.2 $[M+Na]^+$, 388.3 $[M+Na]^+$ HRMS (ES+) 392.3232 $[M+Na]^+$, ($C_{22}H_{43}NNaO_3$ required 392.3141); 390.3023 $[M+Na]^+$, ($C_{22}H_{41}NNaO_3$ required 390.2984); 388.2937 $[M+Na]^+$, ($C_{22}H_{39}NNaO_3$ required 388.2828).

Metharylated Rapeseed Oil (50)[206]



The general procedure for the synthesis of methacrylation of amides was applied using RO rapeseed oil (10 g, 0.01 mol, 1 equiv.), DCM (50 mL), triethylamine (1.99 g, 0.02 mol, 2 equiv) and methacryloyl chloride (2.05 g, 0.02 mol, 2 equiv.) as a light orange oil (77%). ν_{max}/cm^{-1} 3300 (OH), 2914 (C-H), 1736 (C=O), 1170 (C-O); δ_H (400MHz, $CDCl_3$): 6.25 (s, $=CH_2$), 5.62 (s, $=CH_2$), 5.52 – 5.20 (1H, m, OC<u>H</u>), 4.47 – 4.04 (5H, m, OCH_2, OCOC<u>H</u>), 3.79 – 3.29 (m, <u>H</u>COH), 2.33 (6H, m, O=CC<u>H</u>$_2$), 1.95 (3H, s, C<u>H</u>$_3$), 1.79 – 1.54 (O=CCH_2C<u>H</u>$_2$, OCHC<u>H</u>$_2$), 1.47 – 1.22 (54H, m, C<u>H</u>$_2$), 0.90 (9H, t, *J*=6.5, C<u>H</u>$_3$).

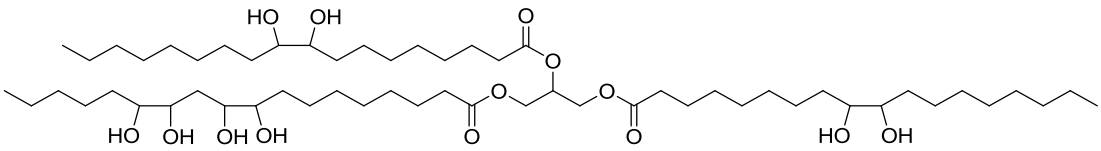
Epoxidation of Rapeseed Oil (52)



Tungsten powder (2.46g, 0.013mol), a solution of H_2O_2 30% w/v (20.9ml, 30g, 0.89mol) and H_2O (9.9ml, 0.62mol) was heated whilst stirring at 50°C for 45 min until dissolved. Orthophosphoric acid (1.78g, 0.018mol) in H_2O (19.8ml, 1.1mol) added to the Tungsten catalyst solution. Rapeseed oil (500g) and Adogen 464

(3.58g) heated gently at 40 °C whilst stirring vigorously with an overhead stirrer. Tungsten catalyst solution added to the triglyceride mix followed by H_2O_2 30% w/v (300ml, 432g, 12.7mol) and H_2O (825ml). The reaction was stirred for 4 h. Reaction mixture dissolved in diethyl ether and water separated off. Organic layer dried over $MgSO_4$ and diethyl ether removed under reduced pressure to give a yellow oil (465.2 g, 86%). ν_{max}/cm^{-1} 2915 (C-H), 1733 (C=O), 1170 (C-O); δ_H (400MHz, $CDCl_3$): 5.33 – 5.20 (1H, m, OC<u>H</u>), 4.22 (2H, dd, *J*=11.5, 4.5, OC<u>H</u>$_2$) 4.07 (2H, dd, *J*=11.5, 5.5, OC<u>H</u>$_2$), 3.25 – 2.79 (8H, m, C<u>H</u>(O)C<u>H</u>), 2.31 (6H, td, *J*=2.5, 7.6, O=CC<u>H</u>$_2$), 1.86 – 1.68 (2H, m, CH(O)CHC<u>H</u>$_2$CH(O)CH), 1.67 – 1.57 (6H, m, O=CCH$_2$C<u>H</u>$_2$), 1.56 – 1.43 (12H, m, CH(O)CHC<u>H</u>$_2$), 1.38 – 1.19 (54H, m, C<u>H</u>$_2$), 1.06 (1H, t, *J*=6.4, CH(O)CHCH$_2$C<u>H</u>$_3$) 0.88 (9H, t, *J*=6.8, C<u>H</u>$_3$); C^{13} (100MHz, $CDCl_3$) δ: 172.92, (3x -<u>C</u>OOR), 68.87 (O<u>C</u>H), 61.97 (2x O<u>C</u>H$_2$), 56.79 – 53.62 (<u>C</u>H(O)<u>C</u>H), 33.81 (3x O=C<u>C</u>H$_2$), 31.79 (<u>C</u>H$_2$CH$_2$CH$_3$), 29.63 – 26.01 (<u>C</u>H$_2$), 24.71 (O=CCH$_2$<u>C</u>H$_2$), 22.59 (<u>C</u>H$_2$CH$_3$) 13.87 (<u>C</u>H$_3$); m/z (ES^+) 969.7365 [M+Na^+] (needed $C_{57}H_{102}NaO_4$ 969.7421).

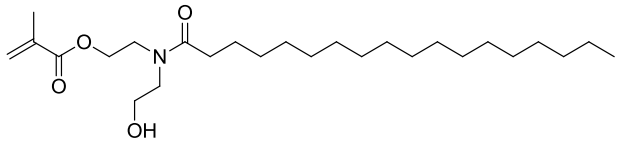
Ring-Opening of Rapeseed Oil (53)[51]



Tungsten powder (12 μm, 99.9%, 1.97 g), a solution of H_2O_2 30% w/v (16.7 mL) and H_2O (7.92 mL) was heated whilst stirring at 50°C for 45 min until dissolved. Orthophosphoric acid (1.42 g) in H_2O (15.8 mL) added to the Tungsten catalyst solution. Rapeseed oil (400 g) and Adogen 464 (2.86 g) heated gently at 40 °C whilst

stirring vigorously with an overhead stirrer. Tungsten catalyst solution added to the triglyceride mix followed by H_2O_2 30% w/v (300 mL), Orthophosphoric acid (150 mL) and H_2O (825 mL). The reaction was heated to 100 °C and stirred for 6 h. Reaction mixture dissolved in diethyl ether and water separated off. Organic layer dried over $MgSO_4$ and diethyl ether removed under reduced pressure to give a yellow oil (465.2 g, 86%). ν_{max}/cm^{-1} 3356 (O-H), 2915, 2846 (C-H), 1733 (C=O), 1170 (C-O); δ_H (400MHz, $CDCl_3$): 5.33 – 5.20 (1H, m, OC<u>H</u>), 4.22 (2H, dd, *J*=11.5, 4.5, OC<u>H</u>$_2$) 4.06 (2H, dd, *J*=11.5, 5.5, OC<u>H</u>$_2$), 2.31 (6H, td, *J*=2.5, 7.6, O=CC<u>H</u>$_2$), 1.86 – 1.68 (2H, m, CH(O)CHC<u>H</u>$_2$CH(O)CH), 1.67 – 1.57 (6H, m, O=CCH$_2$C<u>H</u>$_2$), 1.56 – 1.43 (12H, m, CH(O)CHC<u>H</u>$_2$), 1.38 – 1.19 (54H, m, C<u>H</u>$_2$), 0.88 (9H, t, *J*=6.8, C<u>H</u>$_3$).

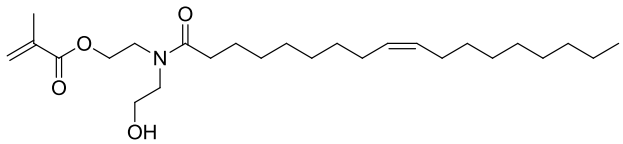
2-(*N*-(2-hydroxyethyl)stearamido)ethyl methcarylate (CB**(58/59)) (2,2'-(stearoylazanediyl)bis(ethane-2,1-diyl) bis(2-methylacrylate))**



The general procedure for the synthesis of methacrylation of amides was applied (7.2.2) using CB**(30)** (100 g, 0.28 mol) DCM (200 mL) triethylamine (28.0 g, 0.29 mol) and methacryloyl chloride (28.9 g, mL, 0.29 mol) to give CB**(58/59)** as an orange solid (86%). ν_{max}/cm^{-1} 3388 (O-H), 2915, 2849 (C-H), 1728, 1629 (C=O), 1159 (C-O), 940, 718 (C=C); δ_H (400MHz, $CDCl_3$): 6.10 (1H, s, =C<u>H</u>$_2$), 5.65 – 5.55 (1H, m,=C<u>H</u>$_2$), 5.39 – 5.30 (1H, m, <u>H</u>C=C<u>H</u>), 4.40 – 4.22 (1H m, OH, OC<u>H</u>$_2$), 3.83 (t, *J*=5.0, HOC<u>H</u>$_2$), 3.80 – 3.73 (m, HOC<u>H</u>$_2$), 3.67 (m, OCH$_2$C<u>H</u>$_2$N), 3.60 – 3.53 (m, NC<u>H</u>$_2$), 3.50 (q, *J*=5.5, NC<u>H</u>$_2$), 2.38 (2H, t, *J*=7.5, O=CCH$_2$), 2.11 – 1.96 (1H, m,

C$\underline{H}_2$CH=), 1.94 (3H, s, C$\underline{H}_3$), 1.68 – 1.53 (2H, m, O=CCH$_2$C$\underline{H}_2$), 1.39 – 1.18 (24H, m, C$\underline{H}_2$), 0.88 (3H, t, *J*=6.5, C$\underline{H}_3$); δ_C (100MHz, $CDCl_3$): 175.69 (C=O), 167.05 (C=O), 135.68 ($\underline{C}$=CH$_2$), 129.96 - 129.75 (H$\underline{C}$=$\underline{C}$H), 125.93 (C=$\underline{C}$H$_2$), 62.51, 62.48 (O$\underline{C}$H$_2$), 61.50, 60.76 HO$\underline{C}$H$_2$), 52.25, 50.61, (N$\underline{C}$H$_2$) 47.78, 45.37 (N$\underline{C}$H$_2$), 33.61 (O=C$\underline{C}$H$_2$), 31.91 ($\underline{C}$H$_2$), 29.75 - 29.31 ($\underline{C}$H$_2$), 27.20 ($\underline{C}$H$_2$), 25.29 ($\underline{C}$H$_2$), 22.67 ($\underline{C}$H$_2$), 18.30 ($\underline{C}$H$_3$), 18.27 ($\underline{C}$H$_3$), 14.10 ($\underline{C}$H$_3$); m/*z* HRMS (ES+) 508.3926 $[M+H]^+$, ($C_{30}H_{54}NO_5$ required 508.3924); 506.3769 $[M+H]^+$, ($C_{30}H_{52}NO_5$ required 506.3767); 480.3614 $[M+H]^+$,($C_{28}H_{50}NO_5$ required 480.3611) 440.3665 $[M+H]^+$, ($C_{26}H_{50}NO_4$ required 440.3662); 438.3508 $[M+H]^+$, ($C_{26}H_{48}NO_4$ required 438.3505); 412.3350 $[M+H]^+$, ($C_{24}H_{46}NO_4$ required 412.3349) 372.3400 $[M+H]^+$, ($C_{22}H_{46}NO_3$ required 372.3399); 370.3244 $[M+H]^+$, ($C_{22}H_{44}NO_3$ required 370.3243); 344.3089 $[M+H]^+$, ($C_{20}H_{42}NO_3$ required 344.3086).

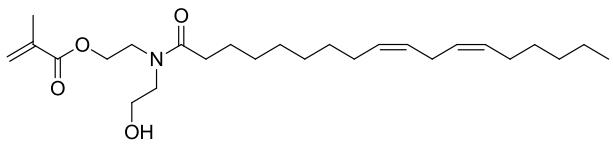
(Z)-2-(*N*-(2-hydroxyethyl)oleamido)ethyl methacrylate (RS**(58/59)) (Z)-2,2'-(oleoylazanediyl)bis(ethane-2,1-diyl) bis(2-methylacrylate)**



The general procedure for the synthesis of methacrylation of amides was applied (7.2.2) using RS**(30)** (100 g, 0.27 mol) DCM (200 mL) triethylamine (28.3 g, 0.28 mol) and methacryloyl chloride (28.5 g, 0.28 mol) to give RS**(58/59)** as an orange solid (89%). ν_{max}/cm^{-1}3394 (OH), 2918, 2850 (C-H), 1721, 1617 (C=O), 1464, 1159, 719 (C=C); δ_H (400MHz, $CDCl_3$): 6.09 (1H, s, =CH$_2$), 5.65 – 5.60 (1H, m, =CH$_2$), 5.43 – 5.26 (2H, m, H$\underline{C}$=C$\underline{H}$), 4.37 – 4.21 (2H, m, OCH$_2$), 3.90 – 3.43 (6H, m,

$NC\underline{H_2}$. $HOC\underline{H_2}$), 2.35 (2H, t, *J*=7.5, $O=CC\underline{H_2}$), 2.08 – 1.95 (7H, m, $=CHC\underline{H_2}$, $C\underline{H_3}$), 1.71 – 1.51 (2H, m, $O=CCH_2C\underline{H_2}$), 1.44 – 1.12 (20H, m, $C\underline{H_2}$), 0.88 (3H, t, *J*=6.5, $C\underline{H_3}$); δ_C (100MHz, $CDCl_3$): 173.02 ($\underline{C}=O$), 166.54 ($\underline{C}=O$), 135.11 ($\underline{C}=CH_2$), 129.35 - 129.13 ($H\underline{C}=\underline{C}H$), 125.78 ($C=\underline{C}H_2$), 61.89, 61.43 ($O\underline{C}H_2$), 60.99 59.64 ($HO\underline{C}H_2$), 50.23, 47.21 ($N\underline{C}H_2$), 44.51 ($N\underline{C}H_2$), 31.28 ($O=C\underline{C}H_2$), 29.14 - 28.49 ($CH_2$), 26.59 ($CH_2$), 24.63 ($CH_2$), 22.06 ($CH_2$), 17.68 ($CH_3$), 13.50 ($CH_3$); m/*z* HRMS (ES+) 506.3763 $[M+H]^+$, ($C_{30}H_{52}NO_5$ required 506.3767); 504.3609 $[M+H]^+$, ($C_{30}H_{50}NO_5$ required 504.3611); 502.3451 $[M+H]^+$,($C_{30}H_{48}NO_5$ required 502.3454) 438.3002 $[M+H]^+$, ($C_{26}H_{48}NO_4$ required 438.3505); 436.3346 $[M+H]^+$, ($C_{26}H_{46}NO_4$ required 436.3349); 434.3190 $[M+H]^+$,($C_{26}H_{44}NO_2$ required 434.3192) 370.3240 $[M+H]^+$, ($C_{22}H_{44}NO_3$ required 370.3243); 368.3084 $[M+H]^+$, ($C_{22}H_{42}NO_3$ required 368.3086); 366.3932 $[M+H]^+$,($C_{22}H_{40}NO_3$ required 366.2930).

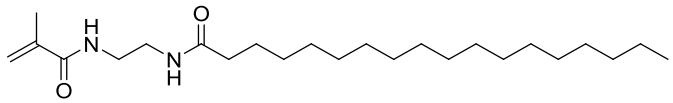
2-((9Z,12Z)-*N*-(2-hydroxyethyl)heptadeca-9,12-dienamido)ethyl methacrylate (SB**(58/59)) (2,2'-((9Z,12Z)-heptadeca-9,12-dienoylazanediyl)bis(ethane-2,1-diyl) bis(2-methylacrylate))**



The general procedure for the synthesis of methacrylation of amides was applied (7.2.2) using SB**(30)** (100 g, 0.27 mol) DCM (200 mL) triethylamine (28.3 g, 0.28 mol) and methacryloyl chloride (25.5 g, 0.28 mol) to give SB**(58/59)** as an orange solid (92%). ν_{max}/cm^{-1} 3403 (OH), 2919, 2850 (C-H), 1721, 1619 (C=O), 1464, 1159, 719 (C=C); δ_H (400 MHz, $CDCl_3$): 6.10 (1H, s, $=C\underline{H_2}$), 5.65 – 5.56 (1H, m, $=C\underline{H_2}$),

5.47 – 5.25 (2H, m, HC=CH), 4.36 – 4.24 (2H, m, OCH_2), 3.84 – 3.73 (2H, m, $HOCH_2$), 3.71 – 3.68 (1H, m, NCH_2), 3.59 – 3.47 (1H m, NCH_2), 2.84 – 2.72 (1H m, $=CHCH_2CH=$), 2.39 (2H, t, *J*=7.5, $O=CCH_2$), 2.14 – 1.96 (4H, m, $=CHCH_2$), 1.94 (3H, s, CH_3),1.68 – 1.53 (2H, m, $O=CCH_2CH_2$), 1.14 – 1.19 (20H, m, CH_2), 0.97 (0.5H, t, *J*=7.5, $=CHCH_2CH_3$) 0.88 (3H,t, *J*=6.8, CH_3); δ_C (100MHz, $CDCl_3$): 175.76 (C=O), 167.23 (C=O), 135.65 ($C=CH_2$), 129.96 - 129.74 (HC=CH), 125.88 ($C=CH_2$), 62.48, 61.99 (OCH_2), 61.33, 60.70 ($HOCH_2$), 52.27, 50.58 (NCH_2), 49.89, 47.75 (NCH_2), 31.92 ($O=CCH_2$), 29.76 – 29.32 (CH_2), 27.21 (CH_2), 25.32 (CH_2), 25.19 (CH_2), 22.69 (CH_2), 18.29 (CH_3), 14.12 (CH_3); m/*z* (ES^+) HRMS (ES+) 506.3767 $[M+H]^+$, ($C_{30}H_{52}NO_5$ required 506.3767); 504.3614 $[M+H]^+$, ($C_{30}H_{50}NO_5$ required 504.3611); 502.3286 $[M+H]^+$, ($C_{30}H_{48}NO_5$ required 502.3454) 438.3503 $[M+H]^+$, ($C_{26}H_{48}NO_4$ required 438.3505); 436.3350 $[M+H]^+$, ($C_{26}H_{46}NO_4$ required 436.3349); 434.3195 $[M+H]^+$,($C_{26}H_{44}NO_4$ required 434.3192) 370.3245 $[M+H]^+$, ($C_{22}H_{44}NO_3$ required 370.3243); 368.3088 $[M+H]^+$, ($C_{22}H_{42}NO_3$ required 368.3086); 366.2933 $[M+H]^+$,($C_{22}H_{40}NO_3$ required 366.2930).

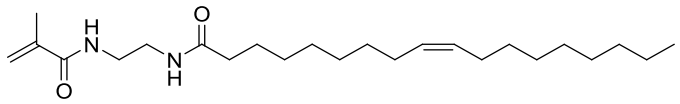
***N*-(2-methacrylamidoethyl)stearamide (**CB**(60a))**



The general procedure for the synthesis of methacrylation of amides was applied (7.2.2) using CB**(61a)** (100 g, 0.32 mol) DCM (500 mL) triethylamine (33.4 g, 0.32 mol) and methacryloyl chloride (33.1 g, 0.32 mol) to give CB**(60a)** as an orange solid, (74%). ν_{max}/cm^{-1} 3298 (N-H), 2916, 2849 (C-H), 1642, 1617 (C=O) 1555 (N-H); δ_H (400MHz, $CDCl_3$): 7.04 (1H, s, NH), 6.65 (1H, s, NH), 5.76 (1H, s, $=CH_2$),

5.42 – 5.28 (3H, m, HC=CH, =CH_2), 3.50 – 3.40 (4H, m, HNCH_2), 2.22 – 2.12 (2H, t, *J*=7.5, O=CCH_2), 2.07 – 1.94 (4H, m, CH_2CH=), 1.95 (3H, s, CH_3), 1.66 – 1.54 (2H, m, O=CCH_2CH_2), 1.39 – 1.20 (~18H, m, CH_2), 0.88 (3H, t, *J*=6.5, CH_3); δ_C (100MHz, $CDCl_3$): 175.02 (HNC=O), 169.31 (HNC=O), 139.34 (C=CH_2), 129.99 - 127.11 (HC=CH), 120.30 (C=CH_2), 40.93 39.57 (HNCH_2), 36.65 (O=CCH_2), 31.91 (CH_2), 29.91 – 29.14 (CH_2), 27.21 (CH_2), 25.77 (CH_2), 22.67 (CH_2CH_3), 18.56 (CH_3), 14.10 (CH_3); m/*z* (ES^+) 415.3 $[M+Na]^+$ HRMS (ES+) 415.3303 $[M+Na]^+$, ($C_{24}H_{44}N_2NaO_2$ required 415.3300); 417.3459 $[M+Na]^+$, ($C_{24}H_{46}N_2NaO_2$ required 417.3457); 398.3147 $[M+Na]^+$,($C_{22}H_{42}N_2NaO_2$ required 389.3144).

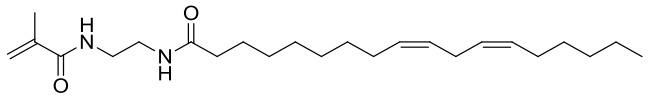
***N*-(2-methacrylamidoethyl)oleamide (**RS**(60a))**



The general procedure for the synthesis of methacrylation of amides was applied (7.2.2) using RS**(61a)** (40 g, 0.12 mol) DCM (100 mL) triethylamine (12.5 g, 17.2 mL, 0.12 mol) and methacryloyl chloride (12.9 g, 12.0 mL, 0.12 mol) to give RS**(60a)** as light yellow waxy solid (80%). ν_{max}/cm^{-1} 3302 (N-H) 2920, 2850 (C-H), 1641, 1617 (C=O), 1555 (N-H), 924, 721 (C=C); δ_H (400MHz, $CDCl_3$): 6.92 (1H, s, NH), 6.46 (1H, s, NH), 5.76 (1H, s, =CH_2), 5.47 – 5.25 (6H, m, HC=CH, =CH_2), 3.50 – 3.41 (4H, m, HNCH_2), 2.86 – 2.72 (2H, m, =HCCH_2CH=), 2.17 (2H, t, *J*=7.5, O=CCH_2), 2.11 – 1.97 (4H, m, CH_2CH=), 1.96 (3H, s, CH_3), 1.67 – 1.54 (2H, m, O=CCH_2CH_2), 1.40 – 1.19 (20H, m, CH_2), 0.97 (0.33H, t, *J*=7.5, =CHCH_2CH_3), 0.88 (3H, t, *J*=6.5, CH_3); δ_C (100MHz, $CDCl_3$): 175.03 (HNC=O), 169.31 (O=CNH), 139.31 (C=CH_2), 130.23 – 127.74 (HC=CH), 120.30 (C=CH_2), 40.91 (HNCH_2),

39.66 (HN$\underline{C}H_2$), 36.67 (O=C$\underline{C}H_2$), 31.90 ($\underline{C}H_2$), 29.72 – 29.14 (C$\underline{H_2}$), 27.22 ($\underline{C}H_2$), 27.19 ($\underline{C}H_2$), 25.74 ($\underline{C}H_2$), 22.58 ($\underline{C}H_2$), 18.55 ($\underline{C}H_3$), 14.11 ($\underline{C}H_3$); m/*z* (ES^+) 415.3 $[M+Na]^+$ HRMS (ES+) 415.3287 $[M+Na]^+$, ($C_{24}H_{44}N_2NaO_2$ required 415.3300); 413.3133 $[M+Na]^+$, ($C_{24}H_{42}N_2NaO_2$ required 413.3144); 411.2980 $[M+Na]^+$,($C_{24}H_{40}N_2NaO_2$ required 411.2987).

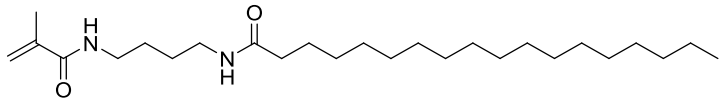
(9Z,12Z)-*N*-(2-methacrylamidoethyl)octadeca-9,12-dienamide (SB**(60a))**



The general procedure for the synthesis of methacrylation of amides was applied (7.2.2) using SB**(61a)** (100 g, 0.31 mol) DCM (200 mL) triethylamine (31.2g, 0.31 mol) and methacryloyl chloride (32.4 g, 0.31 mol) to give SB**(60a)** as an orange solid (90%). ν_{max}/cm^{-1} 3308 (N-H), 2917, 2849 (C-H), 1640, 1617 (C=O), 1559 (N-H), 919, 720 (C=C); δ_H (400MHz, $CDCl_3$): 6.92 (1H, s, N$\underline{H}$), 6.46 (1H, s, N$\underline{H}$), 5.76 (1H, s, =CH_2), 5.47 – 5.25 (6H, m, $\underline{H}$C=C$\underline{H}$, =C$\underline{H_2}$), 3.50 – 3.41 (4H, m, HNC$\underline{H_2}$), 2.86 – 2.72 (2H, m, =HCC$\underline{H_2}$CH=), 2.17 (2H, t, *J*=7.5, O=CC$\underline{H_2}$), 2.11 – 1.97 (4H, m, C$\underline{H_2}$CH=), 1.96 (3H, s, C$\underline{H_3}$), 1.67 – 1.54 (2H, m, O=CCH$_2$C$\underline{H_2}$), 1.40 – 1.19 (20H, m, C$\underline{H_2}$), 0.97 (0.33H, t, *J*=7.5, =CHCH$_2$C$\underline{H_3}$), 0.88 (3H, t, *J*=6.5, C$\underline{H_3}$); δ_C (100MHz, $CDCl_3$): 175.03 (HN$\underline{C}$=O), 169.31 (O=$\underline{C}$NH), 139.31 ($\underline{C}$=CH_2), 130.23 – 127.74 (H$\underline{C}$=$\underline{C}$H), 120.30 (C=$\underline{C}H_2$), 40.91 (HN$\underline{C}H_2$), 39.66 (HN$\underline{C}H_2$), 36.67 (O=C$\underline{C}H_2$), 31.90 ($\underline{C}H_2$), 29.72 – 29.14 (C$\underline{H_2}$), 27.22 ($\underline{C}H_2$), 27.19 ($\underline{C}H_2$), 25.74 ($\underline{C}H_2$), 22.58 ($\underline{C}H_2$), 18.55 ($\underline{C}H_3$), 14.11 ($\underline{C}H_3$); m/*z* (ES^+) 415.3 $[M+Na]^+$ HRMS (ES+) 415.3287 $[M+Na]^+$, ($C_{24}H_{44}N_2NaO_2$ required 415.3300); 413.3141 $[M+Na]^+$,

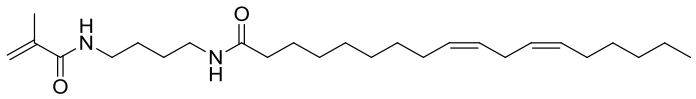
($C_{24}H_{42}N_2NaO_2$ required 413.3144); 411.2980 $[M+Na]^+$, ($C_{24}H_{40}N_2NaO_2$ required 411.2987).

***N*-(4-methacrylamidobutyl)stearamide (**CB**(60b))**



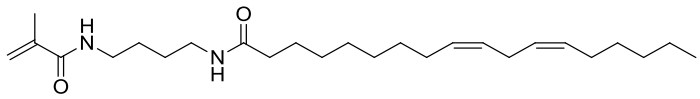
The general procedure for the synthesis of methacrylation of amides was applied (7.2.2) using CB**(61b)** (100 g, 0.29 mol) DCM (200 mL) triethylamine (29.4 g, 0.29 mol) and methacryloyl chloride (30.3 g, 0.29 mol) to give CB**(60b)** as an orange solid (69%). ν_{max}/cm^{-1} 3298 (N-H), 2916, 2849 (C-H), 1642, 1617 (C=O), 1555, 720 (C=C); δ_H (400MHz, CDCl3): 6.14 (1H, s, NH), 5.86 (1H, s, NH), 5.70 (1H, s, =CH$_2$), 5.40 – 5.28 (2H, m, HC=CH, =CH$_2$), 3.34 (2H, q, *J*=6.5 HNCH$_2$), 3.28 (2H, q, *J*=6.5, HNCH$_2$), 2.16 (2H, t, *J*=7.5, O=CCH$_2$), 2.07 – 1.99 (2H, m, CH$_2$CH=), 1.96 (3H, s, CH$_3$), 1.68 – 1.48 (6H, m, CH$_2$), 1.37 – 1.25 (24H, m, CH$_2$), 0.88 (3H, t, *J*=6.8, CH$_3$); δ_C (100MHz, $CDCl_3$): 173.44 (HNC=O), 168.70 (O=CNH), 139.99 (C=CH$_2$), 130.02 (HC=CH), 129.77 (HC=CH), 119.58 (C=CH$_2$), 39.21 (HNCH$_2$), 38.96 (HNCH$_2$), 36.88 (O=CCH$_2$), 31.95 (CH$_2$), 29.78 - 29.18 (CH$_2$), 27.23 (CH$_2$), 27.19 (CH$_2$), 26.98 (CH$_2$), 26.89 (CH$_2$), 25.84 (CH$_2$), 22.72 (CH$_2$), 18.75 (CH$_3$), 14.17 (CH$_3$); m/z (ES^+) 455.4 $[M+Na]^+$ HRMS (ES+) 455.3774 $[M+Na]^+$, ($C_{26}H_{50}N_2NaO_2$ required 455.3770); 443.3616 $[M+Na]^+$, ($C_{26}H_{48}N_2NaO_2$ required 443.3613); $[M+Na]^+$; 417.3459 $[M+Na]^+$, ($C_{24}H_{46}N_2NaO_2$ required 417.3457).

***N*-(4-methacrylamidobutyl)oleamide (**RS**(60b))**



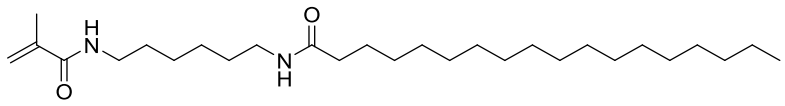
The general procedure for the synthesis of methacrylation of amides was applied (7.2.2) using RS**(61b)** amide (100 g, 0.28 mol) DCM (200 mL) triethylamine (28.7 g, 0.28 mol) and methacryloyl chloride (29.3 g, 0.28 mol) to give RS**(60b)** as an orange solid (91%). ν_{max}/cm^{-1} 3307 (N-H), 2918, 2849 (C-H), 1640 (C=O), 1546, 720 (C=C); δ_H (400MHz, $CDCl_3$): 6.15 (1H, s, NH), 5.86 (1H, s, NH), 5.70 (1H, s, =CH$_2$), 5.47 – 5.20 (5H, m, HC=CH, =CH$_2$), 3.34 (2H, q, *J*=6.5 HNCH$_2$), 3.28 (2H, apparent dd, *J*=11.5, 5.5 HNCH$_2$), 2.82 – 2.75 (1H, m, =HCCH$_2$CH=), 2.16 (2H, t, *J*=7.5, O=CCH$_2$), 2.11 – 1.98 (4H, m, CH$_2$CH=), 1.96 (3H, s, CH$_3$), 1.63 – 1.51 (6H, m, CH$_2$), 1.37 – 1.25 (24H, m, CH$_2$), 0.98 (0.45H, t, *J*=7.5, =CHCH$_2$CH$_3$), 0.88 (3H, t, *J*=6.5, CH$_3$); δ_C (100MHz, $CDCl_3$): 173.44 (HNC=O), 168.70 (O=CNH), 140.05 (C=CH$_2$), 130.24 – 127.91 (HC=CH), 119.47 (C=CH$_2$), 39.21 (NHCH$_2$), 38.96 (NHCH$_2$), 36.84 (O=CCH$_2$), 31.91 (CH$_2$), 29.77 – 29.16 (CH$_2$), 27.22 (CH$_2$), 26.98 (CH$_2$), 26.89 (CH$_2$), 25.80 (CH$_2$), 25.63 (CH$_2$), 22.68 (CH$_2$), 18.71 (CH$_3$), 14.12 (CH$_3$); m/z (ES^+) 421.3 $[M+H]^+$ HRMS (ES+) 421.3711 $[M+H]^+$, ($C_{26}H_{49}N_2O_2$ required 421.3794); 419.3554 $[M+H]^+$, ($C_{26}H_{47}N_2O_2$ required 419.3638); $[M+H]^+$; 417.3399 $[M+H]^+$, ($C_{26}H_{45}N_2O_2$ required 417.3481).

(9Z,12Z)-*N*-(4-methacrylamidobutyl)octadeca-9,12-dienamide (SB**(60b))**



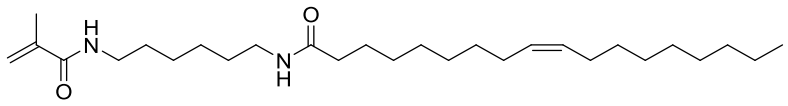
The general procedure for the synthesis of methacrylation of amides was applied (7.2.2) using SB**(61b)** (50 g, 0.14 mol) DCM (100 mL) triethylamine (14.4 g, 0.14 mol) and methacryloyl chloride (14.6 g, 0.14 mol) to give SB**(60b)** as an orange solid, (88%). ν_{max}/cm^{-1} 3300 (N-H), 2919, 2850 (C-H), 1697, 1633 (C=O), 1536, 721 (C=C); δ_H (400MHz, $CDCl_3$): 6.15 (1H, s, NH), 5.86 (1H, s, NH), 5.70 (1H, s, =CH$_2$), 5.47 – 5.20 (5H, m, HC=CH, =CH$_2$), 3.34 (2H, q, *J*=6.5 HNCH$_2$), 3.28 (2H, apparent dd, *J*=11.5, 5.5 HNCH$_2$), 2.82 – 2.75 (1H, m, =HCCH$_2$CH=), 2.16 (2H, t, *J*=7.5, O=CCH$_2$), 2.11 – 1.98 (4H, m, CH$_2$CH=), 1.96 (3H, s, CH$_3$), 1.64 – 1.51 (6H, m, CH$_2$), 1.37 – 1.25 (22H, m, CH$_2$), 0.98 (0.50H, t, *J*=7.5, =CHCH$_2$CH$_3$), 0.88 (3H, t, *J*=6.5, CH$_3$); δ_C (100MHz, $CDCl_3$): 173.44 (HNC=O), 168.70 (O=CNH), 140.05 (C=CH$_2$), 130.24 – 127.91 (HC=CH), 119.47 (C=CH$_2$), 39.21 (NHCH$_2$), 38.96 (NHCH$_2$), 36.84 (O=CCH$_2$), 31.91 (CH$_2$), 29.77 – 29.18 (CH$_2$), 27.25 (CH$_2$), 26.98 (CH$_2$), 26.89 (CH$_2$), 25.82 (CH$_2$), 25.63 (CH$_2$), 22.68 (CH$_2$), 18.71 (CH$_3$), 14.12 (CH$_3$); m/z (ES^+) 443.3 $[M+Na]^+$ HRMS (ES+) 443.3616 $[M+Na]^+$, ($C_{26}H_{48}N_2NaO_2$ required 443.3613); 441.3459 $[M+Na]^+$, ($C_{26}H_{46}N_2NaO_2$ required 441.3457); $[M+Na]^+$; 439.3297 $[M+Na]^+$, ($C_{26}H_{44}N_2NaO_2$ required 439.3300).

***N*-(6-methacrylamidohexyl)stearamide (**CB**(60c))**



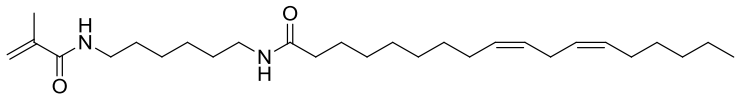
The general procedure for the synthesis of methacrylation of amides was applied (7.2.2) using CB**(61c)** (100 g, 0.27 mol) DCM (200 mL) triethylamine (27.2 g, 0.27 mol) and methacryloyl chloride (28.2 g, 0.27 mol) to give CB**(60c)** as an orange solid (67%). ν_{max}/cm^{-1} 3313 (N-H), 2917, 2850 (C-H), 1634, (C=O), 1533, 719 (C=C); δ_H (400 MHz, CDCl3): 5.96 (1 H, s, NH), 5.68 (2H, s, NH, =CH_2), 5.62 – 5.32 (2H, m, =CH_2, HC=CH, 3.31 (2H, apparent dd, *J*=13.0, 6.5), 3.24 (2H, apparent dd, *J*=13.0, 6.5), 2.16 (2H, t, *J*=7.5, O=CCH_2), 2.04 – 1.97 (3H, m, CH_2CH=), 1.96 (3H, s, CH_3), 1.67 – 1.18 (24H, m, CH_2), 0.88 (3H ,t, *J*=6.8, CH_3); δ_C (100MHz, $CDCl_3$): 173.30 (HNC=O), 168.55 (O=CNH), 140.21 (C=CH_2), 130.00 (HC=CH), 129.71 (HC=CH), 119.22 (C=CH_2), 39.21 (NHCH_2), 38.91 (NHCH_2), 36.78 (O=CCH_2), 31.95 (CH_2), 29.75 – 29.17 (CH_2), 27.19 (CH_2), 27.12 (CH_2), 26.03 (CH_2), 26.06 (CH_2), 25.85 (CH_2), 22.67 (CH_2), 18.72 (CH_3), 14.11 (CH_3); m/z (ES^+) 451.4 $[M+H]^+$ HRMS (ES+) 451.4181 $[M+H]^+$, ($C_{28}H_{55}N_2O_2$ required 451.4264); 449.4032 $[M+H]^+$, ($C_{28}H_{53}N_2O_2$ required 449.4107); $[M+H]^+$; 423.3921 $[M+H]^+$, ($C_{26}H_{51}N_2O_2$ required 423.3951).

***N*-(6-methacrylamidohexyl)oleamide (**RS**(60c))**



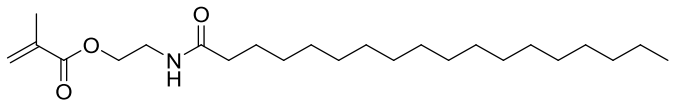
The general procedure for the synthesis of methacrylation of amides was applied (7.2.2) using RS**(61c)** (60 g, 0.15 mol) DCM (120 mL) triethylamine (15.9g, 0.15 mol) and methacryloyl chloride (15.7 g, 0.15 mol) to give RS**(60c)** as an orange solid (87%). ν_{max}/cm^{-1} 3310 (N-H), 2919, 2851 (C-H), ,1634 1609 (C=O), 1530, 721 (C=C); δ_H (400MHz, $CDCl_3$): 6.08 (1H, s, N<u>H</u>), 5.81 (1H, s, N<u>H</u>), 5.68 (1H, s, =C<u>H</u>$_2$), 5.48 – 5.23 (4H, m, <u>H</u>C=C<u>H</u>, =C<u>H</u>$_2$), 3.30 (2H, apparent dd, *J*=13.0, 6.5, NHC<u>H</u>$_2$), 3.23 (2H, apparent, *J*=13.0, 6.5, NHC<u>H</u>$_2$), 2.84 – 2.74 (1H, m, =CHC<u>H</u>$_2$CH=), 2.16 (3H, t, *J*=7.5, O=CC<u>H</u>$_2$), 2.10 – 1.98 (4H, m, C<u>H</u>$_2$CH=), 1.96 (3H, s, C<u>H</u>$_3$), 1.67 – 1.20 (30H, m, C<u>H</u>$_2$), 0.97 (0.40H, t, *J*=7.5, =CHCH$_2$C<u>H</u>$_3$), 0.89 (3H, t, *J*=6.5, C<u>H</u>$_3$); δ_C (100MHz, $CDCl_3$): 173.28 (HN<u>C</u>=O), 168.58 (O=<u>C</u>NH), 140.20 (<u>C</u>=CH$_2$), 130.26 – 127.71 (H<u>C</u>=<u>C</u>H), 119.22 (C=<u>C</u>H$_2$), 39.18 (NH<u>C</u>H$_2$), 38.92 (NH<u>C</u>H$_2$), 36.83 (O=C<u>C</u>H$_2$), 31.89 (<u>C</u>H$_2$), 29.75 – 29.16 (C<u>H</u>$_2$), 27.19 (C<u>H</u>$_2$), 27.17 (<u>C</u>H$_2$), 26.03 (C<u>H</u>$_2$), 26.02 (C<u>H</u>$_2$), 25.84 (<u>C</u>H$_2$), 22.67 (<u>C</u>H$_2$), 18.72 (<u>C</u>H$_3$), 14.11 (<u>C</u>H$_3$); m/z (ES^+) 449.4 $[M+H]^+$ HRMS (ES+) 449.4034 $[M+H]^+$, ($C_{28}H_{53}N_2O_2$ required 449.4107); 447.3874 $[M+H]^+$, ($C_{28}H_{51}N_2O_2$ required 447.3951); $[M+H]^+$; 445.3713 $[M+H]^+$, ($C_{28}H_{49}N_2O_2$ required 445.3794).

(9Z,12Z)-*N*-(6-methacrylamidohexyl)octadeca-9,12-dienamide (SB**(60c))**



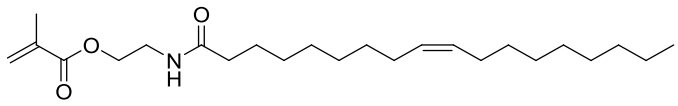
The general procedure for the synthesis of methacrylation of amides was applied (7.2.2) using SB**(61c)** (100 g, 0.26 mol) DCM (200 mL) triethylamine (26.6 g, 0.26 mol) and methacryloyl chloride (27.2 g, 0.26 mol) to give SB**(60c)** as an orange solid (88%). ν_{max}/cm^{-1} 3302 (N-H), 2920, 2850 (C-H), 1641 (C=O), 1555, 721 (C=C); δ_H (400 MHz, $CDCl_3$): 5.99 (1H, s, N<u>H</u>), 5.68 (2H, broad s, =C<u>H</u>$_2$, N<u>H</u>), 5.47 – 5.24 (4H, m, <u>H</u>C=C<u>H</u>, =C<u>H</u>$_2$), 3.31 (2H, apparent dd, *J*=13.0, 6.5, HNC<u>H</u>$_2$), 3.24 (2H, apparent dd, *J*=13.0, 6.5, C<u>H</u>$_2$NH), 2.84 – 2.74 (1H, t, *J*=6.5, =CHC<u>H</u>$_2$CH=), 2.16 (2H, t, *J*=7.5, O=CC<u>H</u>$_2$), 2.07 – 1.98 (4H, m, =CHC<u>H</u>$_2$), 1.96 (3H, s, C<u>H</u>$_3$), 1.68 – 1.21 (26H, m, C<u>H</u>$_2$), 0.98 (0.24H, t, *J*=7.5, =CHCH$_2$C<u>H</u>$_3$), 0.93 – 0.83 (3H, m, C<u>H</u>$_3$); δ_C (100MHz, $CDCl_3$): 173.47 (HN<u>C</u>=O), 168.68 (O=<u>C</u>NH), 140.20 (<u>C</u>=CH$_2$), 130.26 – 127.71 (H<u>C</u>=<u>C</u>H), 119.31 (C=<u>C</u>H$_2$), 39.18 (NH<u>C</u>H$_2$), 38.92 (NH<u>C</u>H$_2$), 36.83 (O=C<u>C</u>H$_2$), 31.89 (<u>C</u>H$_2$), 31.46 (<u>C</u>H$_2$), 29.75 – 29.16 (C<u>H</u>$_2$), 27.19 (<u>C</u>H$_2$), 27.15 (<u>C</u>H$_2$), 26.03 (<u>C</u>H$_2$), 25.84 (<u>C</u>H$_2$), 25.58 (<u>C</u>H$_2$), 22.67 (<u>C</u>H$_2$), 18.72 (<u>C</u>H$_3$), 14.11 (<u>C</u>H$_3$); m/z (ES^+) 449.4 $[M+H]^+$ HRMS (ES+) 449.4033 $[M+H]^+$, ($C_{28}H_{53}N_2O_2$ required 449.4107); 447.3875 $[M+H]^+$, ($C_{28}H_{51}N_2O_2$ required 447.3951); $[M+H]^+$; 445.3719 $[M+H]^+$, ($C_{28}H_{49}N_2O_2$ required 445.3794).

2-stearamidoethyl methacrylate (CB**(60d))**



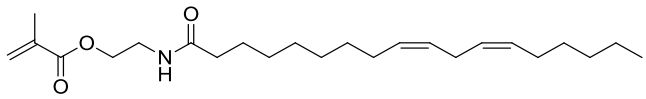
The general procedure for the synthesis of methacrylation of amides was applied (7.2.2) using Cocoa butter ethanolamine amide (34 g, 0.11 mol) DCM (165 mL), triethylamine (11.1 g, 15.3 mL, 0.11 mol) and methacryloyl chloride (11.2 g, 10.5 mL, 0.11 mol) water (2 x 200 mL) $NaHCO_3$ (aq) (2 x 200 mL) to give CB**(60d)** as a cream waxy solid (31.8 g, 77 %). m.p. 30 °C; ν_{max}/cm^{-1} 3292 (N-H), 2916, 2848 (C-H), 1719, 1638 (C=O), 1546 (N-H), 1161 (C-O), 939, 719 (C=C); δ_H (400MHz, $CDCl_3$): 6.13 (1H, s,=C$\underline{H}_2$), 5.85 (1H, s, N$\underline{H}$), 5.60 (1H, s, =C$\underline{H}_2$), 5.38 – 5.31 (2H, m, $\underline{H}$C=C$\underline{H}$), 4.25 (2H, t, *J*=5.5, OC$\underline{H}_2$), 3.57 (2H, apparent dd, *J*=11.0, 5.5, C$\underline{H}_2$NH), 2.18 (2H, t, *J*=7.5, O=CC$\underline{H}_2$), 2.05 – 1.97 (4H m, $\underline{H}_2$CHC=C), 1.95 (3H, s, C$\underline{H}_3$), 1.68 – 1.56 (2H, m, O=CCH$_2$C$\underline{H}_2$), 1.40 – 1.18 (26H, m, C$\underline{H}_2$), 0.88 (3H t, *J*=6.5, C$\underline{H}_3$); δ_C (100MHz, $CDCl_3$): 173.42 (HN$\underline{C}$=O), 167.52 ($\underline{C}$=O), 135.97 ($\underline{C}$=CH$_2$), 130.01, 129.73 (H$\underline{C}$=$\underline{C}$H), 126.11 (C=$\underline{C}$H$_2$), 63.51 (O$\underline{C}$H$_2$), 38.81 ($\underline{C}$H$_2$NH), 36.75 (O=C$\underline{C}$H$_2$), 31.92 ($\underline{C}$H$_2$), 29.69 – 29.18 ($\underline{C}$H$_2$), 27.22 ($\underline{C}$H$_2$), 27.17 ($\underline{C}$H$_2$), 25.69 ($\underline{C}$H$_2$), 22.68 ($\underline{C}$H$_2$), 18.30 ($\underline{C}$H$_3$), 14.11 ($\underline{C}$H$_3$); m/z (ES^+) 344.2556 $[M+Na]^+$, ($C_{24}H_{43}NNaO_3$ required 416.3141); 346.2710 $[M+Na]^+$, ($C_{24}H_{45}NNaO_3$ required 418.3297); 348.2863 $[M+Na]^+$, ($C_{22}H_{41}NNaO_3$ required 390.2984).

(Z)-2-oleamidoethyl methacrylate (RS**(60d))**



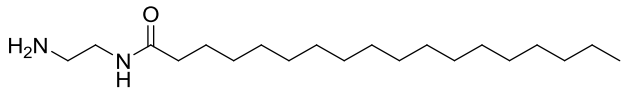
The general procedure for the synthesis of methacrylation of amides was applied (7.2.2) using RS**(61d)** (40 g, 0.12 mol) DCM (80 mL) triethylamine (12.5g, 17.2 ml, 0.12 mol) and methacryloyl chloride (12.9 g, 12.0 mL, 0.12 mol) 5% NaCl (aq) sol^{n} (2 x 100 mL) to give **(**RS**(60d))** as an orange solid (41.2 g, 85%). ν_{max}/cm^{-1} 3294, 2924, 2854 (C-H), 1719, 1654 (C=O), 1542 (N-H), 1160 (C-O), 939, 721 (C=C); δ_H (400MHz, $CDCl_3$): 6.16 (1H, s, NH), 6.12 (2H, s, CH_2), 5.59 (1H, s, CH_2), 5.43 – 5.27 (2H, m, HC=CH), 4.24 (2H, t, *J*=5.5, OCH_2CH_2NH), 3.56 (2H, q, *J*=5.6, OCH_2CH_2NH), 2.84 – 2.72 (2H m, $=HCCH_2CH=$), 2.21 – 2.14 (2H, m, $O=CCH_2$), 2.10 – 1.97 (4H m, $=HCCH_2$), 1.94 (3H s, CH_3), 1.67 – 1.56 (2H, m, $O=CCH_2CH_2$), 1.40 – 1.18 (18H, m, side chain CH_2), 0.97 (2H, t, *J*=7.5 ,CH_3), 0.88 (3H, t, *J*=7.0, CH_3); δ_C (100MHz, $CDCl_3$): 173.47 (HNC=O), 167.43 (O=CO), 135.94 ($C=CH_2$), 130.16 – 127.70 (HC=CH), 126.02 ($C=CH_2$), 63.41 (OCH_2CH_2NH), 38.70 (OCH_2CH_2NH), 36.63 ($O=CCH_2$), 31.87 (CH_2), 31.48 (CH_2), 29.72 – 29.11 (CH_2), 27.17 (CH_2), 25.59 (CH_2), 25.45 (CH_2), 22.64 (CH_2), 18.25 (CH_3), 14.07 (CH_3); m/z (ES^+) 416.3142 $[M+Na]^+$, ($C_{24}H_{43}NNaO_3$ required 416.3141); 414.2987 $[M+Na]^+$, ($C_{24}H_{41}NNaO_3$ required 414.2984**);** 412.2829 $[M+Na]^+$, ($C_{24}H_{39}NNaO_3$ required 412.2828).

2-(9Z,12Z)-octadeca-9,12-dienamidoethyl methacrylate (SB**(60d))**



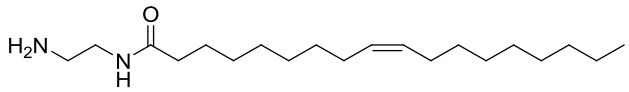
The general procedure for the synthesis of methacrylation of amides was applied (7.2.2) using SB**(61d)** (40 g, 0.12 mol) DCM (400 mL), triethylamine (12.1 g, 0.12 mol) and methacryloyl chloride (12.5 g, 0.12 mol) to give SB**(60d)** as an orange solid (85%). ν_{max}/cm^{-1} 3292 (N-H), 2924, 2854 (C-H), 1719, 1648 (C=O), 1160, 721 (C=C); δ_H (400MHz, $CDCl_3$): 6.12 (1H, s, =C$\underline{H}_2$), 5.97 (1H, broad s, N$\underline{H}$), 5.60 (1H, s, =C$\underline{H}_2$), 5.45 - 5.21 (~3H, m, $\underline{H}$C=C$\underline{H}$), 4.25 (2H, t, *J*=5.5, OC$\underline{H}_2$), 3.57 (2H, q, *J*=5.5, $OCH_2C\underline{H}_2NH$), 2.84 - 2.73 (~1H, m, =HCC$\underline{H}_2$CH=), 2.18 (2H, t, *J*=7.5, O=CC$\underline{H}_2$), 2.10-1.97 (4H, m, =CHC$\underline{H}_2$), 1.95 (3H, s, C$\underline{H}_3$), 1.67-1.57 (2H, m, $O=CCH_2C\underline{H}_2$), 1.39-1.20 (~20H, m, side chain C$\underline{H}_2$), 0.97 (0.22H, t, *J*=7.5 C$\underline{H}_3$), 0.92 – 0.85 (3H, m, C$\underline{H}_3$); δ_C (100MHz, $CDCl_3$): 173.37 (HN$\underline{C}$=O), 167.47 (O=$\underline{C}$O), 135.96 ($\underline{C}$=CH_2), 130.20-127.72 (H$\underline{C}$=$\underline{C}$H), 126.07 (C=$\underline{C}H_2$), 63.48 ($O\underline{C}H_2CH_2NH$), 38.76 ($OCH_2\underline{C}H_2NH$), 36.69 (O=C$\underline{C}H_2$), 31.90 ($\underline{C}H_2$), 31.50 ($\underline{C}H_2$), 29.75 – 29.13 ($\underline{C}H_2$), 27.18 ($\underline{C}H_2$), 25.68 ($\underline{C}H_2$), 22.67 ($\underline{C}H_2$), 22.55($\underline{C}H_2$), 18.28 ($\underline{C}H_3$), 14.06 ($\underline{C}H_3$); m/z (ES^+) 416.3144 $[M+Na]^+$, ($C_{24}H_{43}NNaO_3$ required 416.3141); 414.2987 $[M+Na]^+$, ($C_{24}H_{41}NNaO_3$ required 414.2984); 412.2900 $[M+Na]^+$, ($C_{24}H_{39}NNaO_3$ required 412.2828).

_N_-(2-aminoethyl)stearamide (CB**(61a)) (Synthesised from cocoa butter)**



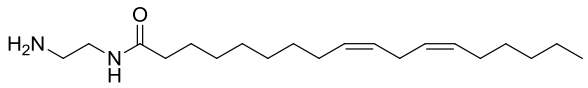
The general procedure for the synthesis of fatty acid amides (7.2.1) was applied using Cocoa butter (100 g, 0.12 mol) heated to 40°C and ethylenediamine (31.5 g, 0.52 mol) heating to 90 °C. Reaction mixture dissolved in chloroform (700 mL) and washed with 15% NaCl $_{(aq)}$ (400 mL) and dried over Na_2SO_4. to give CB**(61a)** as a white solid (63.5 g, 56%). M.p 60 °C; ν_{max}/cm^{-1} 3293 (N-H), 2916, 2848 (C-H), 1631 (C=O), 1543 (N-H); δ_H (400MHz, $CDCl_3$): 5.94 (1H, s, NH), 5.39 – 5.22 (~2H, m, HC=CH), 3.27 (2H, apparent td, *J*=5.8, $HNCH_2$), 2.83 (2H, t, *J*=6.0, CH_2NH), 2.15 (2H, t, *J*=7.5 $O=CCH_2$), 2.05 – 1.91 (~3H, m, $CH_2CH=CH$), 1.68 – 1.51 (2H, m, $O=CCH_2CH_2$), 1.36 – 1.18 (~20H, m, CH_2), 0.88 (3H, t, *J*=6.5, CH_3); δ_C (100MHz, $CDCl_3$): 173.46 (HNC=O), 130.00, 129.76 (HC=CH), 41.93 ($HNCH_2$) 41.45 (H_2CNH_2), 36.90 ($O=CCH_2$), 31.92 (CH_2), 29.77 – 29.16 (CH_2), 27.22 (CH_2), 27.18 (CH_2), 25.82 (CH_2), 22.69 (CH_2), 14.12 (CH_3); m/z (ES^+) 325.2 $[M+H]^+$, 327.3 $[M+H]^+$, 313.3 $[M+H]^+$ HRMS (ES+) 325.3164 $[M+H]^+$ ($C_{20}H_{41}N_2O$ required 325.3219); 327.3224 $[M+H]^+$ ($C_{20}H_{43}N_2O$ required 327.3297); 299.2891 $[M+H]^+$ ($C_{18}H_{39}N_2O$ required 299.2984).

_N_-(2-aminoethyl)oleamide (RS**(61a)) (Synthesised from rapeseed oil)**



The general procedure for the synthesis of fatty acid amides (7.2.1) was applied using rapeseed oil (100 g, 0.11 mol), ethylenediamine (29.7 g, 0.51 mol) and sodium methoxide heating to 90 °C to produce a light yellow waxy solid, (78.7 g, 74%). ν_{max}/cm^{-1} 3299 (N-H), 2918, 2849 (C-H), 1555 (N-H), 1553 (N-H); δ_H (400 MHz, $CDCl_3$); 5.92 (1H, s, N<u>H</u>), 5.43 – 5.22 (3H, m, <u>H</u>C=C<u>H</u>), 3.27 (2H, apparent dd, *J*=11.5, 5.5, C<u>H</u>$_2$NH), 2.80 (2H, t, *J*=7.0 H_2NC<u>H</u>$_2$), 2.86 – 2.70 (1H, m, =CHC<u>H</u>$_2$CH=), 2.15 (2H t, *J*=7.5, O=CC<u>H</u>$_2$), 2.08 – 1.92 (4H, m, =CHC<u>H</u>$_2$), 1.68 – 1.51 (2H, m, O=CCH$_2$C<u>H</u>$_2$), 1.39 – 1.16 (~26H, m, C<u>H</u>$_2$), 0.98 (2H t, *J*=8.0, C<u>H</u>$_3$), 0.89 (3H, t, *J*=6.5, C<u>H</u>$_3$); δ_C (100MHz, $CDCl_3$): 173.60 (HN<u>C</u>=O), 129.61, 127.28 (H<u>C</u>=<u>C</u>H), 41.28 (H_2<u>C</u>NH), 40.80 (H_2N<u>C</u>H$_2$), 36.25 (O=C<u>C</u>H$_2$), 31.28 (<u>C</u>H$_2$), 29.14 - 28.53 (<u>C</u>H$_2$), 26.59 (<u>C</u>H$_2$), 25.17 (<u>C</u>H$_2$), 22.06 (<u>C</u>H$_2$) 13.50 (<u>C</u>H$_3$); m/*z* (ES^+) 325.3212 $[M+H]^+$, ($C_{20}H_{41}N_2O$ required 325.3219 $[M+H]^+$); 323.3056 $[M+H]^+$, ($C_{20}H_{39}N_2O$ required 323.3062 $[M+H]^+$); 321.2899 $[M+H]^+$, ($C_{20}H_{37}N_2O$ required 321.2906 $[M+H]^+$).

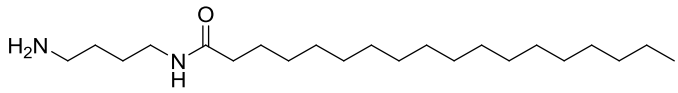
(9Z,12Z)-_N_-(2-aminoethyl)octadeca-9,12-dienamide (SB**(61a)) (Synthesised from soybean oil)**



The general procedure for the synthesis of fatty acid amides (7.2.1) was applied using soybean oil (100 g, 0.11 mol), ethylenediamine (29.7 g, 0.51 mol) and sodium

methoxide heating to 90 °C to produce a light yellow waxy solid. (86.7 g, 81%). m.p 56 °C; ν_{max}/cm^{-1} 3297 (N-H), 2918, 2849 (C-H), 1638 (C=O), 1555 (N-H), 721 (C=C); δ_H (400MHz, $CDCl_3$): 6.00 (2H, s, $N\underline{H}_2$), 5.52 – 5.24 (5H, m, $\underline{H}C=C\underline{H}$), 3.30 (2H, q, *J*=5.5, $C\underline{H}_2NH$), 2.83 (2H, t, *J*=5.5, $H_2NC\underline{H}_2$), 2.77 (2H, t, *J*=6.5, $=CHC\underline{H}_2CH=$), 2.22 – 2.15 (2H, m, $O=CC\underline{H}_2$), 2.11 – 1.97 (4H, m, $=CHC\underline{H}_2$), 1.69 – 1.54 ($O=CCH_2C\underline{H}_2$), 1.45 – 1.18 (~18H, m, $C\underline{H}_2$), 0.98 (1H, t, *J*=7.5, $=CHCH_2C\underline{H}_3$), 0.89 (3H, t, *J*=6.0, $C\underline{H}_3$); δ_C (100MHz, $CDCl_3$):173.44 ($\underline{C}=O$), 131.97-127.12 ($H\underline{C}=\underline{C}H$), 41.93 ($H_2N\underline{C}H_2$), 41.44 ($H_2\underline{C}NH$), 36.86 ($O=C\underline{C}H_2$), 31.91 ($\underline{C}H_2$), 31.53 ($\underline{C}H_2$), 29.77 – 29.16 ($\underline{C}H_2$), 27.20 ($\underline{C}H_2$), 25.80 ($\underline{C}H_2$), 25.63 ($\underline{C}H_2$), 22.68 ($\underline{C}H_2$), 22.57 ($\underline{C}H_2$), 14.09 ($\underline{C}H_3$); m/*z* ($ES^+$) 325.3 $[M+H]^+$ 323.3 $[M+H]^+$ 321.3 $[M+H]^+$; HRMS (ES^+) 325.2905 $[M+H]^+$, ($C_{20}H_{41}N_2O$ required 325.3219); 323.3064 $[M+H]^+$, ($C_{20}H_{39}N_2O$ required 323.3062); 321.2905 $[M+H]^+$, ($C_{20}H_{37}N_2O$ required 320.2906).

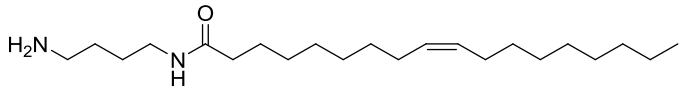
_N_-(4-aminobutyl)stearamide (CB**(61b)) (Synthesised from cocoa butter)**



The general procedure for the synthesis of fatty acid amides (7.2.1) was applied using Cocoa butter (100 g, 0.11 mol), 1,4-diaminobutane (46.1 g, 0.52 mol) and sodium methoxide to produce a light yellow waxy solid (75%). ν_{max}/cm^{-1} 3293 (N-H), 2916, 2848 (C-H), 16381 (C=O), 1543 (N-H), 720 (C=C); δ_H (400MHz, $CDCl_3$): 5.83 (1H, s, NH), 5.44 – 5.26 (1H, m, $\underline{H}C=C\underline{H}$), 3.26 (2H, apparent dd, *J*=12.5, 6.5, $C\underline{H}_2NH$), 2.73 (2H, t, *J*=6.5, $H_2NC\underline{H}_2$), 2.14 (2H, t, *J*=7.5, $O=CC\underline{H}_2$), 2.07 – 1.92 (2H, m, $C\underline{H}_2HC=$), 1.67 – 1.37 (8H, m, $C\underline{H}_2$), 1.35 – 1.18 (26H, m, $C\underline{H}_2$), 0.88 (3H, t, *J*=6.5, $C\underline{H}_3$); δ_C (100MHz, $CDCl_3$): 173.21 (HNC=O), 130.00, 129.76 ($H\underline{C}=\underline{C}H$),

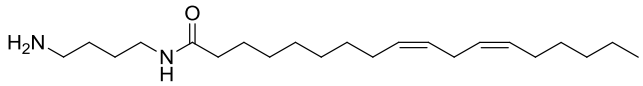
41.73 ($H_2N\underline{C}H_2$), 39.29 ($\underline{C}H_2NH$), 36.92 ($O{=}C\underline{C}H_2$), 31.93 ($\underline{C}H_2$), 30.87 ($\underline{C}H_2$), 29.77 - 29.16 ($\underline{C}H_2$), 27.22 ($\underline{C}H_2$), 27.18 ($\underline{C}H_2$), 27.13 ($\underline{C}H_2$), 25.83 ($\underline{C}H_2$), 22.69 ($\underline{C}H_2$), 14.13 ($\underline{C}H_3$); m/z (ES^+) 377.3506 $[M+Na]^+$, ($C_{22}H_{44}N_2NaO$ required 377.3508); 375.3349 $[M+Na]^+$, ($C_{22}H_{44}N_2NaO$ required 375.3351); 349.3198 $[M+Na]^+$, ($C_{20}H_{40}N_2NaO$ required 349.3195).

_N_-(4-aminobutyl)oleamide (RS**(61b)) (Synthesised from rapeseed oil)**



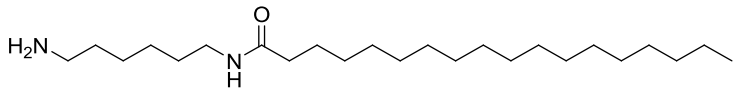
The general procedure for the synthesis of fatty acid amides (7.2.1) was applied using rapeseed oil (100 g, 0.11 mol), 1,4-diaminobutane (44.9 g, 0.51 mol) and sodium methoxide to produce a light yellow waxy solid (82%). ν_{max}/cm^{-1} 3296 (N-H), 2917, 2849 (C-H), 1642 (C=O), 1555 (N-H), 719 (C=C); δ_H (400MHz, $CDCl_3$): 6.08 (1H, s, N$\underline{H}$), 5.48 – 5.21 (3H, m, $\underline{H}C{=}C\underline{H}$), 3.25 (2H, apparent dd, *J*=12.0, 6.5, $C\underline{H}_2NH$), 2.83 – 2.66 (~2H, m, $=CHC\underline{H}_2HC=$), 2.73 (2H, t, *J*=6.5, $H_2NC\underline{H}_2$), 2.15 (2H, t, *J*=7.5, $O{=}CC\underline{H}_2$), 2.09 – 1.94 (4H, m, $\underline{H}_2CHC=$), 1.68 - 1.41 (6H, m, $C\underline{H}_2$), 1.38 – 1.17 (20H, m, $C\underline{H}_2$), 0.98 (~0.30H, t, *J*=7.5, $=CHCH_2C\underline{H}_3$), 0.88 (3H, t, *J*=6.5, $C\underline{H}_3$); δ_C (100MHz, $CDCl_3$): 173.06 ($HN\underline{C}{=}O$), 130.24 – 127.09 ($H\underline{C}{=}\underline{C}H$), 41.69 ($H_2N\underline{C}H_2$), 39.26 ($\underline{C}H_2NH$), 36.85 ($O{=}C\underline{C}H_2$), 31.90 ($\underline{C}H_2$), 31.77 ($\underline{C}H_2$), 30.80 ($\underline{C}H_2$), 29.75 – 29.16 ($\underline{C}H_2$), 27.30 ($\underline{C}H_2$), 27.19 ($\underline{C}H_2$), 25.83 ($\underline{C}H_2$), 25.61 ($\underline{C}H_2$), 22.67 ($\underline{C}H_2$), 14.12 ($\underline{C}H_3$); m/z ($ES^+$); 353.3528 $[M+H]^+$, ($C_{22}H_{45}N_2O$ required 353.3526); 351.3388 $[M+H]^+$, ($C_{22}H_{43}N_2O$ required 351.3370); 349.3214 $[M+H]^+$, ($C_{22}H_{41}N_2O$ required 349.3213).

(9Z,12Z)-*N*-(4-aminobutyl)octadeca-9,12-dienamide (SB**(61b)) (Synthesised from soybean oil)**



The general procedure for the synthesis of fatty acid amides (7.2.1) was applied using soybean oil (100 g 0.11, mol), 1,4-diaminobutane (44.9 g, 0.51 mol) and sodium methoxide to produce a light yellow waxy solid (91%). ν_{max}/cm^{-1} 3299 (N-H), 2918, 2848 (C-H), 1639 (C=O), 1555 (N-H), 721 (C=C); δ_H (400MHz, $CDCl_3$): 5.89 (1H, s, N<u>H</u>), 5.46 – 5.22 (~3H, m, <u>H</u>C=C<u>H</u>), 3.26 (2H, apparent dd, *J*=12.5, 6.5, C<u>H</u>$_2$NH), 2.83 – 2.75 (~2H, m, HC=CHC<u>H</u>$_2$HC=CH), 2.73 (2H, t, *J*=6.5, H_2NC<u>H</u>$_2$), 2.15 (2H, t, *J*=7.5, O=CC<u>H</u>$_2$), 2.09 – 1.97 (4H, m, C<u>H</u>$_2$HC=CH), 1.64 – 1.44 (6H, m, C<u>H</u>$_2$), 1.34 – 1.25 (~22H, m, alkyl C<u>H</u>$_2$), 0.98 (~0.26H, t, *J*=7.5, =CHCH$_2$C<u>H</u>$_3$), 0.89 (3H, t, *J*=6.5, C<u>H</u>$_3$); δ_C (100MHz, $CDCl_3$): 173.09 (HN<u>C</u>=O), 130.23-127.11 (H<u>C</u>=<u>C</u>H), 41.74 (<u>C</u>H$_2$NH$_2$), 39.29 (HN<u>C</u>H$_2$), 36.90 (O=C<u>C</u>H$_2$), 31.91 (<u>C</u>H$_2$), 31.52 (<u>C</u>H$_2$), 31.14 (<u>C</u>H$_2$), 30.89 (<u>C</u>H$_2$), 29.76 – 29.16 (<u>C</u>H$_2$), 27.20 (<u>C</u>H$_2$), 27.12 (<u>C</u>H$_2$), 26.95 (<u>C</u>H$_2$), 25.82 (<u>C</u>H$_2$), 25.63 (<u>C</u>H$_2$), 22.68 (<u>C</u>H$_2$), 22.57 (<u>C</u>H$_2$), 14.12 (<u>C</u>H$_3$); m/z (ES^+); 353.3528 $[M+H]^+$, ($C_{22}H_{45}N_2O$ required 353.3526) 351.3388 $[M+H]^+$, ($C_{22}H_{43}N_2O$ required 351.3370); 349.3214 $[M+H]^+$, ($C_{22}H_{41}N_2O$ required 349.3213).

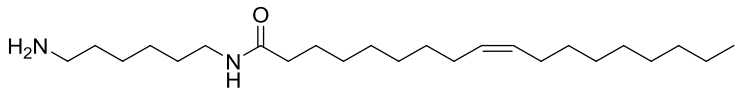
***N*-(6-aminohexyl)stearamide (**CB**(61c)) (Synthesised from cocoa butter)**



The general procedure for the synthesis of fatty acid amides (7.2.1) was applied using cocoa butter (100 g, 0.12 mol), hexamethylenediamine (60.7 g, 0.52 mol) and

sodium methoxide to produce a light yellow waxy solid (80%). ν_{max}/cm^{-1} 3313 (N-H), 2913, 2849 (C-H), 1635 (C=O), 1544 (N-H), 716 (C=C); δ_H (400MHz, $CDCl_3$): 5.55 (1H, s, NH), 5.42 – 5.26 (1H, m, HC=CH), 3.23 (2H, apparent dd, *J*=13.0, 6.5, CH_2NH), 2.68 (2H, t, *J*=6.5, H_2NCH_2), 2.15 (2H, t, *J*=7.5, O=CCH_2), 2.07 – 1.94 (~2H, m, CH_2CH=), 1.70 – 1.56 (2H, m, O=CH_2CH_2), 1.56 – 1.18 (36H, m, CH_2), 0.88 (3H, t, *J*=6.5, CH_3); δ_C (100MHz, $CDCl_3$): 173.15 (HNC=O), 130.00, 129.76 (HC=CH), 42.19 (CH_2NH_2), 39.35 (HNCH_2), 36.93 (O=CCH_2), 33.81 (CH_2), 33.64 (CH_2), 31.94 (CH_2), 29.77 - 29.31 (CH_2), 27.22 (CH_2), 26.78 (CH_2), 26.73 (CH_2), 26.52 (CH_2), 25.86 (CH_2), 22.71 (CH_2), 14.16 (CH_3); m/z (ES^+) 383.3922 $[M+H]^+$, ($C_{24}H_{51}N_2O$ required 383.4001); 381.3766 $[M+H]^+$, ($C_{24}H_{49}N_2O$ required 381.3845); 355.3675 $[M+H]^+$, ($C_{22}H_{47}N_2O$ required 355.3681).

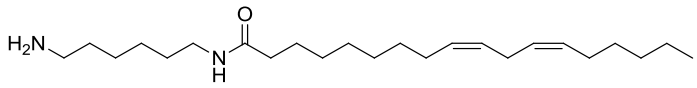
_N_-(6-aminohexyl)oleamide (RS**(61c)) (Synthesised from rapeseed oil)**



The general procedure for the synthesis of fatty acid amides (7.2.1) was applied using rapeseed oil (100 g, 0.11 mol), hexamethylenediamine (59.2 g, 0.52 mol) and sodium methoxide to produce a light yellow waxy solid (86%). ν_{max}/cm^{-1} 3312 (N-H), 2917, 2848 (C-H), 1635 (C=O), 1553 (N-H), 720 (C=C); δ_H (300MHz, $CDCl_3$): 5.56 (1H, s, NH), 5.45 – 5.25 (~3H, m, HC=CH), 3.24 (2H, apparent dd, *J*=13.5, 6.5, CH_2NH), 2.86 – 2.69 (~1H, m, =CHCH_2CH=), 2.68 (2H, t, *J*=6.5, H_2NCH_2), 2.15 (2H, t, *J*=7.5, O=CCH_2), 2.11 – 1.94 (4H, m, =$CHCH_2$), 1.73 – 1.56 (2H, m, O=CCH_2CH_2), 1.57 – 1.18 (~28H, m, CH_2), 0.98 (0.55, t, *J*=7.5, =$CHCH_2CH_3$), 0.88 (3H, t, *J*=6.5, CH_3); δ_C (75 MHz, $CDCl_3$): 172.41 (HNC=O), 129.59 – 127.08

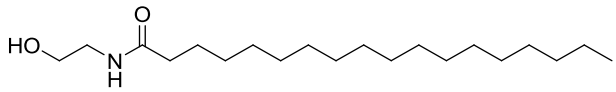
(H<u>C</u>=<u>C</u>H), 41.48 ($H_2N\underline{C}H_2$), 38.72 ($H_2\underline{C}NH$), 36.27 ($O=C\underline{C}H_2$), 33.03 ($\underline{C}H_2$), 31.27 ($\underline{C}H_2$), 29.13 – 28.52 ($\underline{C}H_2$), 26.58 ($\underline{C}H_2$), 26.11 ($\underline{C}H_2$), 25.89 ($\underline{C}H_2$), 25.20 ($\underline{C}H_2$), 24.99 ($\underline{C}H_2$), 22.05 ($\underline{C}H_2$), 13.49 ($\underline{C}H_3$); m/z (ES^+) 381.3765 $[M+H]^+$, ($C_{24}H_{49}N_2O$ required 380.3845); 379.3612 $[M+H]^+$, ($C_{24}H_{47}N_2O$ required 379.3688); 377.3456 $[M+H]^+$, ($C_{24}H_{45}N_2O$ required 377.3532).

(9Z,12Z)-*N*-(6-aminohexyl)octadeca-9,12-dienamide (SB**(61c)) (Synthesised from soybean oil)**



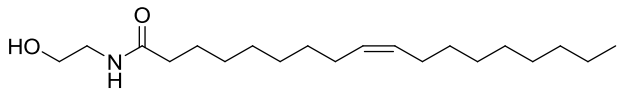
The general procedure for the synthesis of fatty acid amides (7.2.1) was applied using soybean oil (100 g, 0.11 mol), hexamethylenediamine (59.2 g, 0.52 mol) and sodium methoxide to produce a light yellow waxy solid (82%). ν_{max}/cm^{-1} 3297 (N-H), 2918, 2848 (C-H), 1637 (C=O), 1544 (N-H), 721 (C=C); δ_H (400MHz, $CDCl_3$): 5.50 (1H, s, N<u>H</u>), 5.44 - 5.26 (~3H, m, <u>H</u>C=C<u>H</u>), 3.24 (2H, apparent dd, *J*=13.0, 6.5, C<u>H</u>$_2$NH), 2.84 – 2.73 (~1H, m, =CHC<u>H</u>$_2$HC=), 2.68 (2H, t, *J*=6.5, $H_2NC\underline{H}_2$), 2.15 (2H, t, *J*=7.5, O=CC<u>H</u>$_2$), 2.10 – 1.93 (4H, m, C<u>H</u>$_2$HC=), 1.68 – 1.56 (2H, m, $O=CCH_2C\underline{H}_2$), 1.57 – 1.18 (28H, m, C<u>H</u>$_2$), 0.98 (0.33, t, *J*=7.5, $=CHCH_2C\underline{H}_3$), 0.89 (3H, t, J=6.5, C<u>H</u>$_3$); δ_C (100 MHz, $CDCl_3$): 173.31 (HN<u>C</u>=O), 129.60 – 127.58 (H<u>C</u>=<u>C</u>H), 41.48 ($H_2N\underline{C}H_2$), 38.71 ($H_2\underline{C}NH$), 36.31 ($O=C\underline{C}H_2$), 33.01 ($\underline{C}H_2$), 31.26 ($\underline{C}H_2$), 29.14 – 28.52 ($\underline{C}H_2$), 26.58 ($\underline{C}H_2$), 26.11 ($\underline{C}H_2$), 25.89 ($\underline{C}H_2$), 25.21 ($\underline{C}H_2$), 24.99 ($\underline{C}H_2$), 22.05 ($\underline{C}H_2$), 13.55 ($\underline{C}H_3$); m/z (ES^+) 381.3764 $[M+H]^+$, ($C_{24}H_{49}N_2O$ required 381.3845); 379.3612 $[M+H]^+$, ($C_{24}H_{47}N_2O$ required 379.3688); 377.3458 $[M+H]^+$, ($C_{24}H_{45}N_2O$ required 377.3532).

***N*-(2-hydroxyethyl)stearamide (**CB**(61d)) (Synthesis of cocoa butter)**



The general procedure for the synthesis of fatty acid amides (7.2.1) was applied using ethanolamine (3.19 g, 3.15 mL, 0.05 mol, and cocoa butter (10 g, 0.012 mol) and sodium methoxide heated to 110°C. Reaction product dissolved in chloroform (100 mL), washed with 15% NaCl $_{(aq)}$ and dried over Na_2SO_4, to produce CB**(61d)** as a waxy solid, (8.76 g, 82%). ν_{max}/cm^{-1} 3292 (NH, OH broad), 2916 (C-H), 2848, 1641 (C=O), 1560 (NH); δ_H (400MHz, $CDCl_3$): 6.01 (1H, s, N<u>H</u>), 5.42 – 5.26 (2H, m, <u>H</u>C=C<u>H</u>), 3.72 (2H, t, *J*=5.0 HOC<u>H</u>$_2$), 3.42 (2H, apparent dd, *J*=5.5, 10.0, <u>H</u>$_2$CNH),2.61 (1H, s, OH), 2.20 (2H, t, *J*=7.5 O=CC<u>H</u>$_2$), 2.09 – 1.93 (4H, m, =CHC<u>H</u>$_2$), 1.70 – 1.55 (2H, m, O=CCH$_2$C<u>H</u>$_2$), 1.38 – 1.17 (26H, m, C<u>H</u>$_2$), 0.88 (3H t, *J*=6.5, C<u>H</u>$_3$); δ_C (100MHz, $CDCl_3$): 174.61 (HN<u>C</u>=O), 130.03, 129.74 (H<u>C</u>=<u>C</u>H), 62.59 (HO<u>C</u>H$_2$), 42.48 (H$_2$<u>C</u>NH), 36.71 (O=C<u>C</u>H$_2$), 31.94 (<u>C</u>H$_2$), 29.78 - 29.15 (<u>C</u>H$_2$), 27.23 (<u>C</u>H$_2$), 27.18 (<u>C</u>H$_2$), 25.73 (<u>C</u>H$_2$), 22.69 (<u>C</u>H$_2$), 14.13 (<u>C</u>H$_3$); m/z (ES^+) 348.3 $[M+Na]^+$, 350.2 $[M+Na]^+$,322.3 $[M+Na]^+$, HRMS (ES^+) 348.2870 ($C_{20}H_{39}NNaO_2$ required 348.2878); 350.3154 ($C_{20}H_{41}NNaO_2$ required 350.3035); 322.2826 ($C_{18}H_{37}NNaO_2$ required 322.2722).

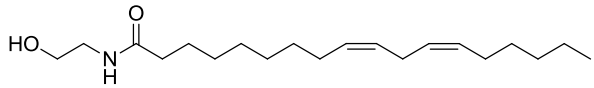
***N*-(2-hydroxyethyl)oleamide (**RS**(61d)) (Synthesised from rapeseed oil)**



The general procedure for the synthesis of fatty amides (7.2.1) was applied using ethanolamine (31.1 g, 0.51 mol, and rapeseed oil (100 g, 0.11 mol) heated to 110°C.

Reaction product dissolved in diethyl ether (600 mL), washed with 5% $NaCl_{(aq)}$ (300 mL) to produce RS**(61d)** as an orange waxy solid (103.2 g, 97%). M.p. 38-42°C; ν_{max}/cm^{-1} 3297 (N-H, O-H broad), 2918, 2849 (C-H), 1642 (C=O), 1560 (N-H); δ_H (400MHz, $CDCl_3$) δ:6.15 (1H, s, NH), 5.46- 5.25 (3H, m, HC=CH), 3.71 (2H, t, *J*=5.0, $HOCH_2$), 3.41 (2H, apparent dd, *J*=10.0, 5.5, CH_2NH), 3.18 (1H, broad s, OH), 2.86 - 2.71 (1H, m, $=CHCH_2CH=$), 2.20 (2H, t, *J*=7.5, $O=CCH_2$), 2.11 - 1.94 (4H, m, $=CHCH_2$), 1.70 – 1.54 (2H, m, $O=CCH_2CH_2$), 1.42 – 1.21 (20H, m, CH_2), 0.98 (~0.35H, t, *J*=7.5, $=CHCH_2CH_3$), 0.88 (3H, t, *J*=6.5 CH_3); δ_C (100MHz, $CDCl_3$): 174.59 (HNC=O), 130.03 - 127.11 (HC=CH), 62.37 ($HOCH_2$), 42.44 (H_2CNH), 36.68 ($O=CCH_2$), 31.91 (CH_2), 29.77 - 29.15 (CH_2), 27.23 (CH_2), 27.18 (CH_2), 25.73 (CH_2), 22.58 (CH_2), 14.12 (CH_3); m/z (ES^+) 344.3 $[M+Na]^+$, 346.4 $[M+Na]^+$, 348.3 $[M+Na]^+$ HRMS (ES^+) 344.2556 $[M+Na]^+$, ($C_{20}H_{35}NNaO_2$ required 344.2560); 346.2710 $[M+Na]^+$, ($C_{20}H_{37}NNaO_2$ required 346.2117); 348.2863 $[M+Na]^+$, ($C_{20}H_{39}NNaO_2$ required 348.2873).

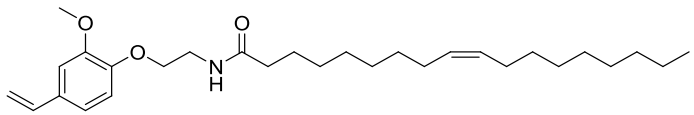
(9Z,12Z)-*N*-(2-hydroxyethyl)octadeca-9,12-dienamide (SB**(61d)) (Synthesised from soyabean oil)**



The general procedure for the synthesis of fatty acid amides (7.2.1) was applied using soybean oil (100 g, 0.11 mol), ethanolamine (31.1 g, 0.51 mol) and sodium methoxide heating to 110 °C. Reaction product dissolved in diethyl ether (600 mL) to produce a light yellow waxy solid (95.3 g, 89%). m.p 40 °C; ν_{max}/cm^{-1} 3297 (NH, OH), 2918, 2849 (C-H), 1642 (C=O), 1555 (N-H), 1035, 722 (C=C); δ_H (300MHz,

$CDCl_3$): 6.11 (1H, s, NH), 5.46-5.24 (~3H, m, HC=CH), 3.71 (2H, t, *J*=5.0 $HOCH_2$), 3.41 (2H, apparent dd, *J*=5.5, 10.0, CH_2NH), 3.09 – 2.77 (1H, broad s, OH), 2.77 (~1H, t, *J*=6.5, $HC=CHCH_2CH=CH$), 2.20 (2H, t, *J*=7.5, $O=CCH_2$), 2.11 - 1.93 (4H, m, $CH_2HC=CH$), 1.69 – 1.56 (2H, m, $O=CCH_2CH_2$), 1.40 - 1.21 (18H, m, CH_2), 0.98 (~0.3H, t, *J*=7.5, $=CHCH_2CH_3$), 0.89 (3H, t, *J*=6.5, CH_3); δ_C (75MHz, $CDCl_3$): 173.94 (HNC=O), 131.35-126.48 (HC=CH), 61.78 ($HOCH_2$), 41.81 (H_2CNH), 36.05 ($O=CCH_2$), 31.28 (CH_2), 30.89 (CH_2) 29.08 – 28.52 (CH_2), 26.57 (CH_2), 25.09 (CH_2), 25.00 (CH_2), 22.05 (CH_2) 21.94 (CH_2), 13.45 (CH_3); m/z (ES^+) 344.2556 $[M+Na]^+$, ($C_{20}H_{35}NNaO_2$ required 344.2560); 346.2710 $[M+Na]^+$, ($C_{20}H_{37}NNaO_2$ required 346.2117); 348.2873 $[M+Na]^+$, ($C_{20}H_{39}NNaO_2$ required 348.2878).

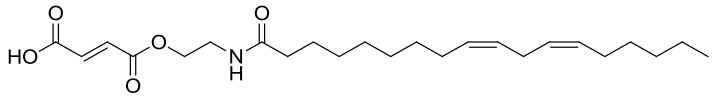
***N*-(2-(2-methoxy-4-vinylphenoxy)ethyl)oleamide (**RS**(68d))**



RS**(61d)** (2.26 g, 6.99 mmol, 1 equiv.), 2-methoxy-4-vinylphenol (1.05 g, 0.95 mL, 6.99 mmol, 1 equiv.), and triphenylphosphine (3.27 g, 0.01 mol, 2 equiv.) dissolved in THF (8 mL). Reaction mixture cooled to 0 °C in an icebath and DIAD (2.63 g, 2.56 mL, 0.1 mol, 2 equiv.) added dropwise under a nitrogen atmosphere. Reaction mixture allowed to warm to room temperature. Mixture dissolved in diethyl ether and triphenylphosphine oxide precipitated and removed *via* filtration. The resulting organics washed with water (2 X 50 mL) and dried over Na_2SO_4, filtered and dried in *vacuo* to produce crude product. Crude product purified using column chromatography (pet ether/EtOAc, 2:1) to give RS**(68d)** (18%) as a cream waxy solid. $R_{f\,=}$ 0.35 (pet ether/EtOAc, 2:1); ν_{max}/cm^{-1} 3297 (NH), 2922, 2852 (C-H), 1697

(C=O), 1262, 1033 (C-O) 989, 721 (C=C); δ_H (400MHz, $CDCl_3$): 6.98-6.85 (3H, m, 3xAr<u>H</u>), 6.65 (1H, dd, *J*=17.6, 10.9, H_2C=C<u>H</u>C), 6.14 (1H, s, N<u>H</u>), 5.63 (1H, d, *J*=17.2, <u>H_2</u>C=CHC), 5.42-5.26 (~3H, m, <u>H</u>C=C<u>H</u>), 5.17 (1H, d, *J*=11.1, <u>H_2</u>C=CHC), 4.09 (2H, t, *J*=5.1, OC<u>H_2</u>CH_2NH), 3.90 (3H, s, C<u>H_3</u>O), 3.66 (2H, q, *J*=10.4, 5.4, OCH_2C<u>H_2</u>NH), 2.76 (~1H, t, *J*=6.5, HC=CHC<u>H_2</u>CH=CH), 2.19 (2H, t, *J*=7.6, O=CC<u>H_2</u>), 2.09-1.97 (4H, m, <u>H_2</u>CCH=CH), 1.68-1.59 (2H, m, O=CCH_2C<u>H_2</u>), 1.38-1.24 (~20H, m, C<u>H_2</u>), 0.97 (~1H, t, *J*=7.5, =CH_2CH_2C<u>H_3</u>), 0.88 (3H, td, *J*=6.9, 3.6, CH_2CH_2C<u>H_3</u>); δ_C (100MHz, $CDCl_3$): 173.32 (HN<u>C</u>=O), 149.67 (<u>C</u>OCH_3), 147.81 (<u>C</u>OCH_2), 136.34 (H_2C=<u>C</u>HC), 131.93 (H_2C=CH<u>C</u>), 130.23 - 127.72 (H<u>C</u>=<u>C</u>H), 119.58 (<u>Ar</u>), 114.50 (<u>Ar</u>), 112.43 (H_2<u>C</u>=CHC), 109.18 (<u>Ar</u>), 68.96 (O<u>C</u>H_2), 55.82 (O<u>C</u>H_3), 38.79 (<u>C</u>H_2NH), 36.79 (O=C<u>C</u>H_2), 31.94 (<u>C</u>H_2), 31.53 (<u>C</u>H_2), 29.77 – 29.15 (<u>C</u>H_2), 27.21 (<u>C</u>H_2), 25.69 (<u>C</u>H_2), 22.69 (<u>C</u>H_2), 22.58 (<u>C</u>H_2), 14.14 (<u>C</u>H_3); m/z (ES^+) 457.3 $[M+H]^+$ HRMS (ES+) 456.3400 $[M+H]^+$, ($C_{29}H_{46}NO_3$ required 456.3478); 457.3559 $[M+H]^+$, ($C_{29}H_{47}NO_3$ required 457.3556); $[M+H]^+$; 341.3618 $[M+H]^+$, ($C_{21}H_{35}$NNaO required 340.2616).

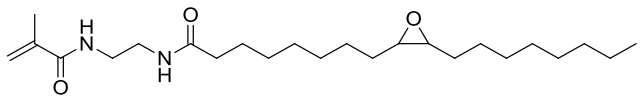
4-(2-(9Z,12Z)-octadeca-9,12-dienamidoethoxy)-4-oxobut-2-enoic acid (RS**(70a))**



Amide (1eq) heated to 80 °C. Maleic anhydride (1.5eq) added and dissolved. Triphenylphosphine and hydroquinone added and reacted at 80 °C for 10h. Reaction mixture dissolved in chloroform and washed with sat. NaCl (aq) to give **(**RS**(70a))** as a brown oil (64%). ν_{max}/cm^{-1}3297 (N-H), 2915 (C-H), 1733 (C=O), 1170 (C-O); δ_H (400MHz, $CDCl_3$): 6.63 (1H, m, N<u>H</u>), 6.30 (1H, d, *J*=12.0, CH=C<u>H</u>C=O), 6.19 (1H,

d, *J*=12.0, CH=CHC=O), 5.40 – 5.16 (4H, m, HC=CH), 4.24 (2H, t, *J*=5.0, OCH_2), 3.50 (2H, apparent dd, *J*=10.5, 5.5, CH_2NH), 2.78 – 2.61 (2H, m, $=CHCH_2CH=$), 2.14 (2H, t, *J*=7.5, $O=CCH_2$), 2.04-1.80 (4H, m, $CH_2CH=$), 1.61-1.38 (2H, m, $O=CCH_2CH_2$), 1.37-1.09 (22H, m, CH_2), 0.90 (0.46H, t, *J*=7.5, $=CHCH_2CH_3$), 0.88 (3H, t, *J*=6.5, CH_3); δ_C (100MHz, $CDCl_3$): 175.33 (HNC=O), 166.89 (OC=O), 168.71 (HOC=O), 131.99-127.11 (HC=CH), 64.27 (OCH_2), 38.51 (CH_2NH), 36.44 ($O=CCH_2$), 31.91 (CH_2), 29.76 – 29.17 (CH_2), 27.20 (CH_2), 25.70 (CH_2), 22.68 (CH_2), 22.57 (CH_2), 14.08 (CH_3); m/z (ES^+) 424.3 [$M+H^+$]; 422.2 [$M+H^+$]; 420.2 HRMS (ES+) 424.2990 [$M+H^+$] ($C_{24}H_{42}NO_5$ required 424.33063); 422.2830 [$M+H^+$] ($C_{24}H_{40}NO_5$ required 421.2906); 420.2678 [$M+H^+$] ($C_{24}H_{38}NO_5$ required 419.2750).

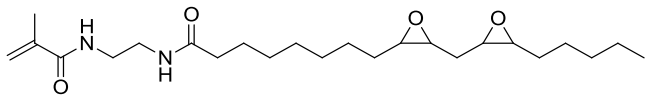
***N*-(2-methacrylamidoethyl)-8-(3-octyloxiran-2-yl)octanamide (**CB**(71a))**



The general procedure for the synthesis of fully epoxidised monomers was applied (7.2.3) using CB**(60a)** (50 g, 0.13 mol), mCPBA (11.2 g, 0.07 mol) and DCM (500 mL) to produce a white solid (61%). ν_{max}/cm^{-1} 3304 (N-H), 2917, 2849 (C-H), 1642 , 1617 (C=O), 1555 (N-H); δ_H (400 MHz, $CDCl_3$) 6.89 (1H, broad s, NH), 6.36 (1H, broad s, NH), 5.75 (1H, s, $=CH_2$), 5.34 (1H, s, $=CH_2$), 3.47 – 3.41 (4H, m, $NHCH_2$), 2.93 – 2.88 (1H, m, HCOCH), 2.18 (2H, t, *J*=7.6, $O=CH_2$), 1.96 (3H, s, CH_3), 1.66 – 1.56 (2H, m, $O=CH_2CH_2$), 1.53 – 1.43 (H, m, $HCOCHCH_2$), 1.38 – 1.21 (30H, m, side chain CH_2) 0.88 (3H, t, *J*=6.5, CH_3); δ_C (100MHz, $CDCl_3$): 175.07 (HNC=O), 169.27 (HNC=O), 139.27 ($C=CH_2$), 120.36 ($=CH_2$), 57.30 (HC(O)CH), 57.27

(HCO)CH), 41.02 (NHCH$_2$), 39.68 (NHCH$_2$), 36.72 (O=CCH$_2$), 31.95 (CH$_2$), 29.68 – 29.15 (CH$_2$), 27.85 (CH$_2$), 26.62 (CH$_2$), 25.78 (CH$_2$), 25.68 (CH$_2$), 22.69 (CH$_2$), 18.59 (CH$_3$), 14.16 (CH$_3$); m/z (ES$^+$) 431.3 [M+Na]$^+$ HRMS (ES+) 431.3253 [M+Na]$^+$, ($C_{24}H_{44}N_2NaO_3$ required 431.3250); 417.3459 [M+Na]$^+$, ($C_{24}H_{46}N_2NaO_2$ required 417.3457); [M+Na]$^+$; 431.3253 [M+Na]$^+$, ($C_{22}H_{42}N_2NaO_2$ required 431.3250).

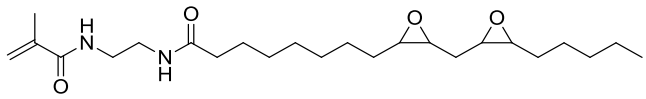
***N*-(2-methacrylamidoethyl)-8-(3-((3-pentyloxiran-2-yl)methyl)oxiran-2-yl)octanamide (**RS**(71a))**



The general procedure for the synthesis of fully epoxidised monomers was applied (7.2.3) using RS**(60a)** (40.0 g, 0.10 mol), mCPBA (26.4 g, 0.15 mol) and DCM (400 mL) to produce a white solid (78%). δ_H (400 MHz, $CDCl_3$): 6.97 (1H, s, NH), 6.56 (1H, s, NH), 5.76 (1H, s, =CH$_2$), 5.34 (1H, s, =CH$_2$), 3.49 – 3.36 (4H, m, HNCH$_2$), 3.23 – 2.84 (3H, m, HC(O)CH), 2.18 (2H, t, *J*=7.5, O=CCH$_2$), 1.96 (s, 3H, CH$_3$), 1.70 – 1.19 (26H, m, CH$_2$), 1.06 (0.35H, t, *J*=7.5, (O)CHCH$_2$CH$_3$), 0.88 (3H, t, *J*=6.5, CH$_3$); δ_C (100MHz, $CDCl_3$): 175.05 (HNC=O), 169.24 (HNC=O), 139.27 (C=CH$_2$), 120.19 (=CH$_2$), 57.24 (HC(O)CH), 57.21 (HC(O)CH), 56.35 (HC(O)CH), 56.22 (HC(O)CH), 41.02 (HNCH$_2$), 39.67 (HNCH$_2$), 36.58 (O=CCH$_2$), 31.84 (CH$_2$), 29.64 – 29.12 (CH$_2$), 27.83 (CH$_2$), 27.47 (CH$_2$), 26.59 (CH$_2$), 25.67 (CH$_2$), 22.64 (CH$_2$), 18.56 (CH$_3$), 14.09 (CH$_3$); m/z (ES$^+$) 459.3 [M+Na]$^+$ HRMS (ES+) 459.2836 [M+Na]$^+$, ($C_{24}H_{40}N_2NaO_5$ required 459.2835); 445.3043 [M+Na]$^+$, ($C_{24}H_{42}N_2NaO_4$

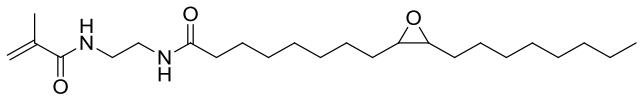
required 445.3042); $[M+Na]^+$; 431.3251 $[M+Na]^+$, ($C_{24}H_{44}N_2NaO_3$ required 431.3250).

***N*-(2-methacrylamidoethyl)-8-(3-((3-pentyloxiran-2-yl)methyl)oxiran-2-yl)octanamide (**SB**(71a))**



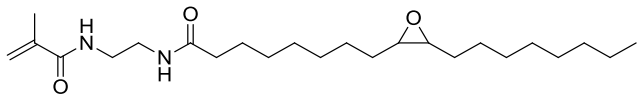
The general procedure for the synthesis of fully epoxidised monomers was applied (7.2.3) using SB**(60a)** (35.0 g, 0.09 mol), mCPBA (30.8 g, 0.18mol) and DCM (350 mL) to produce a white solid (89%). ν_{max}/cm^{-1} 3301 (N-H), 2918, 2849 (C-H), 1642, 1618 (C=O), 1555, 1236; δ_H (400 MHz, $CDCl_3$): 6.89 (1H, s, NH), 6.58 (1H, s, NH), 5.75 (1H, s, =CH_2), 5.36 (1H, s, =CH_2), 3.47 – 3.35 (4H, m, HNCH_2), 3.32 – 2.85 (3H, m, HC(O)CH), 2.18 (2H, t, *J*=7.5, O=CCH_2), 1.96 (s, 3H, CH_3), 1.71 – 1.18 (26H, m, CH_2), 1.06 (0.40H, t, *J*=7.5, =CHCH_2CH_3), 0.88 (3H, t, *J*=6.5, CH_3); δ_C (100MHz, $CDCl_3$) δ: 175.07 (HNC=O), 169.23 (HNC=O), 139.28 (C=CH_2), 120.19 (=CH_2), 57.25 (HC(O)CH), 57.20 (HC(O)CH), 56.35 (HC(O)CH), 56.24 (HC(O)CH), 41.05 (HNCH_2), 39.68 (HNCH_2), 36.61 (O=CCH_2), 31.85 (CH_2), 29.63 – 29.15 (CH_2), 27.83 (CH_2), 27.47 (CH_2), 26.59 (CH_2), 25.67 (CH_2), 22.67 (CH_2), 22.56 (CH_2), 18.57 (CH_3), 14.05 (CH_3); m/z (ES^+) 459.3 $[M+Na]^+$ HRMS (ES+) 459.2832 $[M+Na]^+$, ($C_{24}H_{40}N_2NaO_5$ required 459.2835); 445.3040 $[M+Na]^+$, ($C_{24}H_{42}N_2NaO_4$ required 445.3042); $[M+Na]^+$; 431.3248 $[M+Na]^+$, ($C_{24}H_{44}N_2NaO_3$ required 431.3250).

***N*-(2-methacrylamidoethyl)-8-(3-octyloxiran-2-yl)octanamide (**PECB**(71a))**



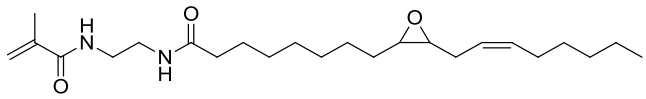
The general procedure for the synthesis of partially epoxidised monomers was applied (7.2.4) using CB**(60a)** (20.0 g, 0.05 mol), mCPBA (0.89 g, 0.005 mol) and DCM (200 mL) to produce a white solid (65%). ν_{max}/cm^{-1} 3304 (N-H), 2923, 2852 (C-H), 1654, 1618 (C=O), 1551, 721 (C=C); δ_H (400MHz, $CDCl_3$): 6.84 (1H, s, NH), 6.29 (1H, s, NH), 5.76 (1H, s, =CH_2), 5.43 – 5.29 (2H, s, =CH_2, HC=CH), 3.47 – 3.42 (4H, m, HNCH_2), 2.90 (1H, s, CH(O)CH), 2.18 (2H, t, *J*=7.5, O=CCH_2), 2.10 – 1.97 (2H, m, CH_2CH=), 1.96 (3H, s, CH_3), 1.67 – 1.54 (2H, m, O=CCH$_2$CH_2), 1.52 – 1.44 (1H, m, CH_2CH(O)CHCH_2), 1.38 – 1.15 (26H, m CH_2), 0.88 (3H, t, *J*=6.8, CH_3); δ_C (100MHz, $CDCl_3$): 175.17 (HNC=O), 169.40 (O=CNH), 139.25 (C=CH_2), 130.03 (HC=CH), 129.70 (HC=CH), 120.36 (C=CH_2), 57.29 (CH_2CH(O)CHCH_2), 41.03 (HNCH_2), 39.70 (HNCH_2), 36.74 (O=CCH_2), 31.92 (CH_2), 29.76 - 29.13 (CH_2), 27.21 (CH_2), 27.17 (CH_2), 25.77 (CH_2), 22.68 (CH_2), 18.55 (CH_3), 14.11 (CH_3); m/z HRMS (ES^+) 409.3356 $[M+H]^+$, ($C_{24}H_{45}N_2O_3$ required 409.3430); 395.3555 $[M+H]^+$, ($C_{24}H_{47}N_2O_2$ required 395.3638); 393.3400 $[M+H]^+$, ($C_{24}H_{45}N_2O_2$ required 393.3481); 367.3242 $[M+H]^+$ ($C_{22}H_{43}N_2O_2$ required 367.3325).

***N*-(2-methacrylamidoethyl)-8-(3-octyloxiran-2-yl)octanamide (**PERS**(71a))**



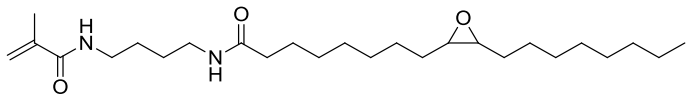
The general procedure for the synthesis of partially epoxidised monomers was applied (7.2.4) using RS**(60a)** (25.0 g, 0.06 mol), mCPBA (8.25 g, 0.05mol) and DCM (250 mL) to produce a yellow solid (87%). ν_{max}/cm^{-1} 3307 (N-H), 2918, 2850 (C-H), 1658, 1618 (C=O), 1553, 720 (C=C); δ_H (400MHz, $CDCl_3$); 7.13 (1H, s, NH), 6.79 (1H, s, NH), 5.77 (1H, s, $=CH_2$), 5.58 – 5.22 (4H, s, $=CH_2$, HC=CH), 3.51 – 3.42 (4H, m, $HNCH_2$), 3.15 - 2.70 (~1H, s, $CH_2CH(O)CHCH_2$), 2.19 (2H, t, *J*=7.6, $O=CCH_2$), 2.09 – 1.98 (4H, m, $CH_2CH=$), 1.96 (3H, s, CH_3), 1.68 – 1.12 (24H, m, CH_2), 1.09 – 0.95 (0.35H, m, $=CHCH_2CH_3$), 0.88 (3H, t, *J*=6.8, CH_3); δ_C (100MHz, $CDCl_3$): 174.80 ($HNC=O$), 169.40 ($O=CNH$), 139.25 ($C=CH_2$), 130.03, 129.70 ($HC=CH$), 120.42 ($C=CH_2$), 57.28, 57.25 ($CH_2CH(O)CHCH_2$), 40.79, 39.57 ($HNCH_2$), 36.53 ($O=CCH_2$), 31.83 (CH_2), 29.76 - 29.11 (CH_2), 27.80 (CH_2), 27.75 (CH_2), 26.58 (CH_2), 25.67 (CH_2), 22.63 (CH_2), 18.53 (CH_3), 14.08 (CH_3); m/z HRMS (ES^+) 445.3040 $[M+Na]^+$, ($C_{24}H_{42}N_2NaO_4$ required 445.3042); 431.3248 $[M+Na]^+$, ($C_{24}H_{44}N_2NaO_3$ required 31.3250); 429.3090 $[M+Na]^+$, ($C_{24}H_{42}N_2NaO_3$ required 429.3093); 415.3298 $[M+Na]^+$, ($C_{24}H_{44}N_2NaO_2$ required 415.3300); 413.3140 $[M+Na]^+$, ($C_{24}H_{42}N_2NaO_2$ required 413.3144.).

(Z)-*N*-(2-methacrylamidoethyl)-8-(3-(oct-2-enyl)oxiran-2-yl)octanamide (PESB**(71a))**



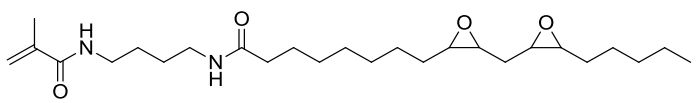
The general procedure for the synthesis of partially epoxidised monomers was applied (7.2.4) using SB**(60a)** (38.0 g, 0.09 mol), mCPBA (16.7 g, 0.09 mol) and DCM (380 mL) to produce a yellow solid (90%). ν_{max}/cm^{-1} 3301 (N-H), 2918, 2850 (C-H), 1658, 1617 (C=O), 1555, 719 (C=C); δ_H (400MHz, $CDCl_3$): 6.92 (1H, s, N<u>H</u>), 6.45 (1H, s, N<u>H</u>), 5.76 (1H, s, =C<u>H</u>$_2$), 5.65 – 5.21 (3H, m =C<u>H</u>$_2$, <u>H</u>C=C<u>H</u>), 3.51 – 3.42 (4H, m, HNC<u>H</u>$_2$), 3.25 – 2.64 (1H, s, $CH_2C\underline{H}(O)CHCH_2$), 2.18 (2H, t, *J*=7.5, O=CC<u>H</u>$_2$), 2.10 – 1.97 (4H, m, C<u>H</u>$_2$CH=), 1.95 (3H, s, C<u>H</u>$_3$), 1.70 – 1.09 (26H, m, C<u>H</u>$_2$), 1.09 – 0.96 (0.40, m, =CHC<u>H</u>$_2$CH$_3$) 0.88 (3H, t, *J*=6.8, C<u>H</u>$_3$); δ_C (100MHz, $CDCl_3$): 175.09 (HN<u>C</u>=O), 169.34 (O=<u>C</u>NH), 139.30 (<u>C</u>=CH$_2$), 132.78 (H<u>C</u>=<u>C</u>H), 132.57 (H<u>C</u>=<u>C</u>H), 130.03 (H<u>C</u>=<u>C</u>H), 129.70 (H<u>C</u>=<u>C</u>H), 120.32 (C=<u>C</u>H$_2$), 57.29 (<u>C</u>H(O)<u>C</u>H), 57.20 (<u>C</u>H(O)<u>C</u>H), 56.61 (<u>C</u>H(O)<u>C</u>H), 54.36 (<u>C</u>H(O)<u>C</u>H), 40.81 (HN<u>C</u>H$_2$), 39.60 (HN<u>C</u>H$_2$), 36.68 (O=C<u>C</u>H$_2$), 31.92 (<u>C</u>H$_2$), 31.66 (<u>C</u>H$_2$), 29.76 - 29.13 (<u>C</u>H$_2$), 27.83 (<u>C</u>H$_2$), 27.40 (<u>C</u>H$_2$), 27.17 (<u>C</u>H$_2$), 26.21 (<u>C</u>H$_2$), 25.77 (<u>C</u>H$_2$), 25.65 (<u>C</u>H$_2$), 22.68 (<u>C</u>H$_2$), 22.55 (<u>C</u>H$_2$), 18.55 (<u>C</u>H$_3$), 14.11 (<u>C</u>H$_3$); m/z HRMS (ES^+) 459.2833 ($C_{24}H_{40}N_2NaO_5$ required 459.2835); 445.3041 $[M+Na]^+$, ($C_{24}H_{42}N_2NaO_4$ required 445.3042); 431.3248 $[M+Na]^+$, ($C_{24}H_{44}N_2NaO_3$ required 431.3250); 429.3091 $[M+Na]^+$, ($C_{24}H_{42}N_2NaO_3$ required 429.3093); 415.3297 $[M+Na]^+$, ($C_{24}H_{44}N_2NaO_2$ required 415.3300); 413.3141 $[M+Na]^+$, ($C_{24}H_{42}N_2NaO_2$ required 413.3144.).

***N*-(4-methacrylamidobutyl)-8-(3-octyloxiran-2-yl)octanamide (**CB**(71b))**



The general procedure for the synthesis of fully epoxidised monomers was applied (7.2.3) using CB**(60b)** (30.5 g, 0.07 mol), mCPBA (6.39 g, 0.04 mol) and DCM (300 mL) to produce a white solid (62%). ν_{max}/cm^{-1} 3300 (N-H), 2918, 2849 (C-H), 1642, 1617 (C=O), 1554, 1235; δ_H (400MHz, $CDCl_3$): 6.15 (1H, s, N<u>H</u>), 5.87 (1H, m, N<u>H</u>), 5.70 (1H, s, =C<u>H</u>$_2$), 5.37 – 5.30 (1H, m, =C<u>H</u>$_2$), 3.35 (2H, q, *J*=6.5, NHC<u>H</u>$_2$), 3.28 (2H, q, *J*=6.5, NHC<u>H</u>$_2$), 2.90 (1H, s, CH_2C<u>H</u>(O)C<u>H</u>CH_2), 2.17 (2H, t, *J*=7.5, O=CC<u>H</u>$_2$), 1.97 (3H, s, C<u>H</u>$_3$), 1.66 –1.20 (34H, m, C<u>H</u>$_2$), 0.88 (3H, t, *J*=6.8, C<u>H</u>$_3$); δ_C (100MHz, $CDCl_3$): 173.55 (HN<u>C</u>=O), 168.98 (O=<u>C</u>NH), 139.98 (<u>C</u>=CH_2), 119.60 (C=<u>C</u>H$_2$), 57.30 (<u>C</u>H(O)<u>C</u>H), 39.21 (NH<u>C</u>H$_2$), 38.95 (NH<u>C</u>H$_2$), 36.88 (O=C<u>C</u>H$_2$), 31.95 (<u>C</u>H$_2$), 29.72 – 29.19 (<u>C</u>H$_2$), 27.85 (<u>C</u>H$_2$), 26.96 (<u>C</u>H$_2$), 26.88 (<u>C</u>H$_2$), 26.62 (<u>C</u>H$_2$), 25.84 (<u>C</u>H$_2$), 22.72 (<u>C</u>H$_2$), 22.69 (<u>C</u>H$_2$), 18.74 (<u>C</u>H$_3$), 14.17 (<u>C</u>H$_3$); m/z (ES^+) 459.3 $[M+Na]^+$ HRMS (ES+) 459.3560 $[M+Na]^+$, ($C_{26}H_{48}N_2NaO_3$ required 459.3563); 417.3455 $[M+Na]^+$, ($C_{26}H_{46}N_2NaO_2$ required 417.3457); $[M+Na]^+$; 417.3454 $[M+Na]^+$, ($C_{26}H_{46}N_2NaO_2$ required 417.3457).

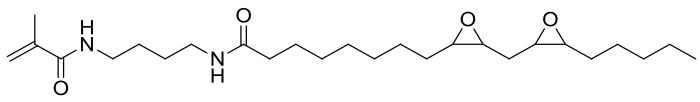
***N*-(4-methacrylamidobutyl)-8-(3-((3-pentyloxiran-2-yl)methyl)oxiran-2-yl)octanamide (**RS**(71b))**



The general procedure for the synthesis of fully epoxidised monomers was applied (7.2.3) using RS**(60b)** (40.0 g, 0.10 mol), mCPBA (24.6 g, 0.14 mol) and DCM (400

mL) to produce a white solid (79%). ν_{max}/cm^{-1} 3302 (N-H), 2919, 2849 (C-H), 1632, 1610 (C=O), 1547, 716 (C=C); δ_H (400MHz, $CDCl_3$): 6.15 (1H, s, NH), 5.86 (1H, m, NH), 5.71 (1H, s, $=CH_2$), 5.33 (1H, s, $=CH_2$), 3.34 (2H, q, *J*=6.5, $NHCH_2$), 3.28 (2H, q, *J*=6.5, $O=CNHCH_2$), 3.14 – 2.88 (3H, m, $CH_2CH(O)CHCH_2$), 2.16 (2H, t, *J*=7.5, $O=CCH_2$), 1.95 (3H, s, CH_3), 1.71 - 1.20 (30H, m, CH_2), 1.06 (0.33H, t, *J*=7.5, $=CHCH_2CH_3$) 0.88 (3H, t, *J*=6.8, CH_3); δ_C (100MHz, $CDCl_3$): 173.45 (HNC=O), 168.98 (O=CNH), 139.97 ($C=CH_2$), 119.59 ($C=CH_2$), 57.30 (CH(O)CH), 39.21 ($NHCH_2$), 38.97 ($NHCH_2$), 36.75 ($O=CCH_2$), 31.94 (CH_2), 31.87 (CH_2), 29.71 – 29.19 (CH_2), 27.85 (CH_2), 26.97 (CH_2), 26.86 (CH_2), 26.64 (CH_2), 25.83 (CH_2), 22.72 (CH_2), 22.67 (CH_2), 18.75 (CH_3), 14.08 (CH_3); m/z (ES^+) 487.3 $[M+Na]^+$ HRMS (ES+) 487.3147 $[M+Na]^+$, ($C_{26}H_{44}N_2NaO_3$ required 487.3148); 473.3354 $[M+Na]^+$, ($C_{26}H_{46}N_2NaO_4$ required 473.3355); $[M+Na]^+$; 459.3562 $[M+Na]^+$, ($C_{26}H_{48}N_2NaO_3$ required 459.3563).

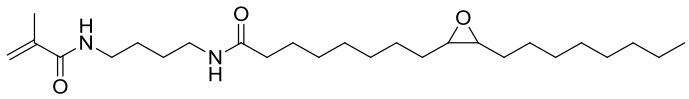
_N_-(4-methacrylamidobutyl)-8-(3-((3-pentyloxiran-2-yl)methyl)oxiran-2-yl)octanamide (SB**(71b))**



The general procedure for the synthesis of fully epoxidised monomers was applied (7.2.3) using SB**(60b)** (30.0 g, 0.07 mol), mCPBA (24.7 g, 0.14 mol) and DCM (300 mL) to produce a white solid (89%). ν_{max}/cm^{-1} 3299 (N-H), 2917, 2848 (C-H), 1635, 1604 (C=O), 1537; δ_H (400 MHz, $CDCl_3$): 6.46 (1H, s, NH), 6.26 (1H, s, NH), 5.70 (1H, s, $=CH_2$), 5.34 – 5.29 (1H, m, $=CH_2$), 3.32 (2H, q, *J*=6.5, $NHCH_2$), 3.26 (2H, apparent dd, *J*=11.5, 5.5 $NHCH_2$), 3.15 – 2.85 (~5H, m, HC(O)CH), 2.17 (3H, t,

J=7.5, O=CCH$_2$), 1.96 (3H, s, CH$_3$), 1.79 – 1.22 (26H, m), 0.94 – 0.84 (3H, m, C<u>H</u>$_3$); δ_C (100MHz, CDCl$_3$): 173.39 (HN<u>C</u>=O), 168.94 (O=<u>C</u>NH), 139.96 (<u>C</u>=CH$_2$), 119.61 (C=<u>C</u>H$_2$), 57.30 (<u>C</u>H(O)<u>C</u>H), 39.23 (NH<u>C</u>H$_2$), 38.96 (NH<u>C</u>H$_2$), 36.88 (O=C<u>C</u>H$_2$), 31.95 (<u>C</u>H$_2$), 31.88 (<u>C</u>H$_2$), 29.72 – 29.19 (<u>C</u>H$_2$), 27.85 (<u>C</u>H$_2$), 26.96 (<u>C</u>H$_2$), 26.88 (<u>C</u>H$_2$), 26.62 (<u>C</u>H$_2$), 25.84 (<u>C</u>H$_2$), 25.64 (<u>C</u>H$_2$) 22.72 (<u>C</u>H$_2$), 22.69 (<u>C</u>H$_2$), 18.69 (<u>C</u>H$_3$), 14.14 (<u>C</u>H$_3$); m/z (ES$^+$) 487.3 [M+Na]$^+$ HRMS (ES+) 487.3147 [M+Na]$^+$, ($C_{26}H_{44}N_2NaO_3$ required 487.3148); 473.3354 [M+Na]$^+$, ($C_{26}H_{46}N_2NaO_4$ required 473.3355); [M+Na]$^+$; 459.3562 [M+Na]$^+$, ($C_{26}H_{48}N_2NaO_3$ required 459.3563).

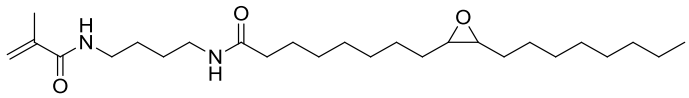
_N_-(4-methacrylamidobutyl)-8-(3-octyloxiran-2-yl)octanamide (PECB**(71b))**



The general procedure for the synthesis of partially epoxidised monomers was applied (7.2.4) using CB**(60b)** (30 g, 0.07 mol), mCPBA (1.26 g, 0.007 mol) and DCM (300 mL) to produce a white solid (60%). ν_{max}/cm^{-1} 3302 (N-H), 2918, 2850 (C-H), 1634, 1605 (C=O), 1537; δ_H (400 MHz, CDCl$_3$): 6.36 (1H, s, N<u>H</u>), 6.13 (1H, s, N<u>H</u>), 5.70 (1H, s, =C<u>H</u>$_2$), 5.39 – 5.26 (2H, m, <u>H</u>C=C<u>H</u>, =C<u>H</u>$_2$), 3.33 (2H, q, *J*=6.5, HNC<u>H</u>$_2$), 3.27 (2H, dd, *J*=12.5, 6.5, HNC<u>H</u>$_2$), 2.90 (1H, s, C<u>H</u>(O)CH), 2.16 (2H, t, *J*=7.5, O=CC<u>H</u>$_2$), 2.06 - 197 (2H, m, CH$_2$CH=), 1.96 (3H, s, C<u>H</u>$_3$), 1.68 – 1.48 (10H, m, CH$_2$), 1.41 – 1.17 (30H, m, C<u>H</u>$_2$), 0.88 (3H, t, *J*=6.7, C<u>H</u>$_3$); δ_C (100 MHz, CDCl$_3$): 173.57 (HN<u>C</u>=O), 168.74 (O=<u>C</u>NH), 139.99 (<u>C</u>=CH$_2$), 129.98 (H<u>C</u>=<u>C</u>H), 129.72 (H<u>C</u>=<u>C</u>H), 119.51 (C=<u>C</u>H$_2$), 57.26 (<u>C</u>H(O)<u>C</u>H), 39.24 (HN<u>C</u>H$_2$), 38.95 (HN<u>C</u>H$_2$), 36.80 (O=C<u>C</u>H$_2$), 31.91 (<u>C</u>H$_2$), 29.69 - 29.16 (<u>C</u>H$_2$), 27.20 (<u>C</u>H$_2$), 27.17 (<u>C</u>H$_2$), 26.98 (<u>C</u>H$_2$), 26.86 (<u>C</u>H$_2$), 25.84 (<u>C</u>H$_2$), 22.68 (<u>C</u>H$_2$CH$_3$), 18.72 (<u>C</u>H$_3$), 14.12

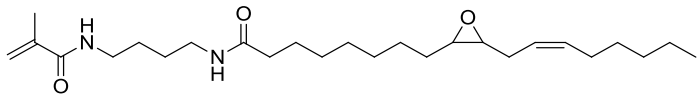
($\underline{C}H_3$); m/z (ES^+) HRMS (ES+) 437.3668 $[M+H]^+$, ($C_{26}H_{49}N_2O_3$ required 437.3743); 421.3714 $[M+H]^+$, ($C_{26}H_{49}N_2O_2$ required 421.3794); 423.3870 $[M+H]^+$, ($C_{26}H_{51}N_2O_2$ required 423.3951); 395.3561 $[M+H]^+$ ($C_{24}H_{47}N_2O_2$ required 395.3638).

_N_-(4-methacrylamidobutyl)-8-(3-octyloxiran-2-yl)octanamide (PERS**(71b))**



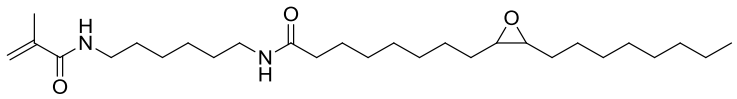
The general procedure for the synthesis of partially epoxidised monomers was applied (7.2.4) using RS**(60b)** (35.0 g, 0.08 mol), mCPBA (10.8 g, 0.06 mol) and DCM (350 mL) to produce a yellow solid (79%). ν_{max}/cm^{-1} 3302 (N-H), 2919, 2850 (C-H), 1634, 1604 (C=O), 1537, 721 (C=C); δ_H (400 MHz, $CDCl_3$): 6.30 (1H, s, N$\underline{H}$), 6.07 (1H, s, N$\underline{H}$), 5.70 (1H, s, =C$\underline{H}_2$), 5.63 – 5.24 (2H, m, $\underline{H}$C=C$\underline{H}$, =C$\underline{H}_2$), 3.33 (2H, q, *J*=6.5, HNC$\underline{H}_2$), 3.27 (2H, apparent dd, *J*=11.5, 5.5, HNC$\underline{H}_2$), 3.20 – 2.73 (3H, m, C$\underline{H}$(O)CH), 2.17 (2H, t, *J*=7.5, O=CC$\underline{H}_2$), 2.10 – 1.98 (2H, m, CH_2CH=), 1.96 (3H, s, C$\underline{H}_3$), 1.68 – 1.19 (30H, m, C$\underline{H}_2$), 1.09 – 0.95 (0.71H, m, =CHCH_2CH_3), 0.88 (3H, t, *J* 6.7, C$\underline{H}_3$); δ_C (100 MHz, $CDCl_3$): 173.50 (HN$\underline{C}$=O), 168.60 (O=$\underline{C}$NH), 140.01 ($\underline{C}$=CH_2), 130.76 (H$\underline{C}$=$\underline{C}$H), 129.98 (H$\underline{C}$=$\underline{C}$H), 128.02 (H$\underline{C}$=$\underline{C}$H), 127.88 (H$\underline{C}$=$\underline{C}$H), 119.24 (C=$\underline{C}H_2$), 57.26 ($\underline{C}$H(O)$\underline{C}$H), 56.38 ($\underline{C}$H(O)$\underline{C}$H) 39.23 (HN$\underline{C}H_2$), 38.95 (HN$\underline{C}H_2$), 36.62 (O=C$\underline{C}H_2$), 31.91 ($\underline{C}H_2$), 29.69 - 29.16 ($\underline{C}H_2$), 27.17 ($\underline{C}H_2$), 26.98 ($\underline{C}H_2$), 25.60 ($\underline{C}H_2$), 25.57 ($\underline{C}H_2$), 22.68 ($\underline{C}H_2$), 18.72 ($\underline{C}H_3$), 14.12 ($\underline{C}H_3$); m/z (ES^+) 473.3 $[M+Na]^+$, 471.2 $[M+Na]^+$, 459.3 $[M+Na]^+$, 457.3 $[M+Na]^+$, 443.3 $[M+Na]^+$, 441.3 $[M+Na]^+$.

(Z)-*N*-(4-methacrylamidobutyl)-8-(3-(oct-2-enyl)oxiran-2-yl)octanamide (PESB**(71b))**



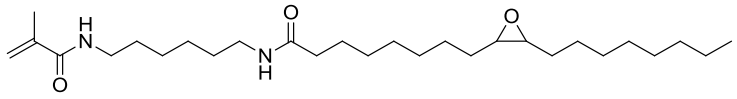
The general procedure for the synthesis of partially epoxidised monomers was applied (7.2.4) using SB**(60b)** (20.0 g, 0.05 mol), mCPBA (8.22 g, 0.05 mol) and DCM (200 mL) to produce a yellow solid (89%). ν_{max}/cm^{-1} 3298 (N-H), 2918, 2850 (C-H), 1634, 1617 (C=O), 1537, 721 (C=C); δ_H (400 MHz, $CDCl_3$): 6.14 (1H, s, NH), 5.87 (1H, s, NH), 5.70 (1H, s, =CH_2), 5.61 – 5.25 (3H, m, HC=CH, =CH_2), 3.34 (2H, q, *J*=6.5, HNCH_2), 3.28 (2H, apparent dd, *J*=12.4, 6.0, HNCH_2), 3.16 – 2.73 (3H, s, CH(O)CH), 2.16 (2H, t, *J*=7.5, O=CCH_2), 2.10 – 1.98 (2H, m, CH_2CH=), 1.97 (3H, s, CH_3), 1.68 – 1.17 (30H, m, CH_2), 1.09 – 0.95 (0.54H, m, =CHCH_2CH_3), 0.88 (3H, t, *J* =6.7, CH_3); δ_C (100 MHz, $CDCl_3$) 173.57 (HNC=O), 168.74 (O=CNH), 139.99 (C=CH_2), 129.98 (HC=CH), 129.72 (HC=CH), 119.51 (C=CH_2), 57.26 (CH(O)CH) 56.64 (CH(O)CH), 39.24 (HNCH_2), 38.95 (HNCH_2), 36.80 (O=CCH_2), 31.90 (CH_2), 29.69 - 29.23 (CH_2), 27.82 (CH_2), 26.98 (CH_2), 26.86 (CH_2), 25.84 (CH_2), 22.65 (CH_2), 18.74 (CH_3), 14.11 (CH_3); m/z (ES^+) 473.3 $[M+Na]^+$, 471.2 $[M+Na]^+$, 459.3 $[M+Na]^+$, 457.3 $[M+Na]^+$, 443.3 $[M+Na]^+$, 441.3 $[M+Na]^+$, 439.3 $[M+Na]^+$.

***N*-(6-methacrylamidohexyl)-8-(3-octyloxiran-2-yl)octanamide (**CB**(71c))**



The general procedure for the synthesis of fully epoxidised monomers was applied (7.2.3) using CB**(60c)** (30.0 g, 0.07 mol), mCPBA (5.89 g, 0.03 mol) and DCM (300 mL) to produce a white solid (60%). ν_{max}/cm^{-1}3301 (N-H), 2918, 2851 (C-H), 1697, 1634 (C=O), 1505; δ_H (400 MHz, $CDCl_3$): 5.98 (1H, s, N<u>H</u>), 5.71 – 5.63 (2H, m, N<u>H</u>, =C<u>H</u>$_2$), 5.38 – 5.27 (1H, m, =C<u>H</u>$_2$), 3.31 (2H, apparent dd, *J*=13.0, 7.0, HNC<u>H</u>$_2$), 3.24 (2H, apparent dd, *J*=13.0, 7.0, HNC<u>H</u>$_2$), 2.95 – 2.85 (~1H, m, <u>H</u>C(O)C<u>H</u>), 2.16 (3H, t, *J*=7.5, O=CC<u>H</u>$_2$), 1.97 (3H, s, C<u>H</u>$_3$), 1.68 – 1.16 (42H, m, C<u>H</u>$_2$), 0.87 (3H, t, *J*=6.5, C<u>H</u>$_3$); δ_C (100MHz, $CDCl_3$): 173.25 (HN<u>C</u>=O), 168.71 (HN<u>C</u>=O), 140.18 (<u>C</u>=CH$_2$), 119.28 (=<u>C</u>H$_2$), 57.27 (H<u>C</u>(O)<u>C</u>H), 56.55 (H<u>C</u>(O)<u>C</u>H), 39.15 (HN<u>C</u>H$_2$), 38.92 (HN<u>C</u>H$_2$), 36.74 (O=C<u>C</u>H$_2$), 31.84 (<u>C</u>H$_2$), 29.65 - 29.19 (<u>C</u>H$_2$), 27.84 (<u>C</u>H$_2$), 27.27 (<u>C</u>H$_2$), 26.85 (<u>C</u>H$_2$), 26.79 (<u>C</u>H$_2$), 25.76 (<u>C</u>H$_2$), 18.75 (<u>C</u>H$_3$), 14.17 (<u>C</u>H$_3$); m/z (ES^+) 487.3 $[M+Na]^+$ HRMS (ES+) 487.3870 $[M+Na]^+$, ($C_{28}H_{52}N_2NaO_3$ required 487.3876); 743.4080 $[M+Na]^+$, ($C_{28}H_{54}N_2NaO_2$ required 473.4083); $[M+Na]^+$; 445.3766 $[M+Na]^+$, ($C_{26}H_{50}N_2NaO_2$ required 445.3770).

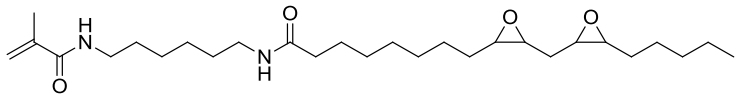
***N*-(6-methacrylamidohexyl)-8-(3-octyloxiran-2-yl)octanamide (**RS**(71c))**



The general procedure for the synthesis of fully epoxidised monomers was applied (7.2.3) using RS**(60c)** (25.0 g, 0.06 mol), mCPBA (14.4 g, 0.08 mol) and DCM (250 mL) to produce a white solid (86%). ν_{max}/cm^{-1} 3309 (N-H), 2917, 2848 (C-H), 1632,

1610 (C=O), 1553; δ_H (400MHz, $CDCl_3$): 6.00 (1H, s, NH), 5.68 (2H, s, NH, =CH_2), 5.31 (1H, s, =CH_2), 3.30 (2H, apparent dd, *J*=13.0, 6.5, HNCH_2), 3.24 (2H, apparent dd, *J*=13.0, 6.5, HNCH_2), 3.20 – 2.75 (3H, m, HC(O)CH), 2.16 (3H, t, *J*=7.5, O=CCH_2), 1.96 (3H s, CH_3), 1.69 – 1.22 (48H, m, CH_2), 1.06 (0.33H, t, *J*=7.5, =CHCH_2CH_3), 0.93 – 0.85 (3H, m, CH_3); δ_C (100MHz, $CDCl_3$): 173.19 (HNC=O), 168.56 (HNC=O), 140.21 (C=CH_2), 119.22 (=CH_2), 57.25 (HC(O)CH), 56.58 (HC(O)CH), 39.17 (HNCH_2), 38.93 (HNCH_2), 36.80 (O=CCH_2), 31.85 (CH_2), 29.65 - 29.19 (CH_2), 27.84 (CH_2), 27.79 (CH_2), 26.60 (CH_2), 26.03 (CH_2), 25.76 (CH_2), 22.66 (CH_2), 18.73 (CH_3), 14.11 (CH_3); m/z (ES^+) 515.3 $[M+Na]^+$ HRMS (ES+) 515.3460 $[M+Na]^+$, ($C_{28}H_{48}N_2NaO_5$ required 515.3461); 501.3667 $[M+Na]^+$, ($C_{28}H_{50}N_2NaO_4$ required 501.3668); $[M+Na]^+$; 487.7137 $[M+Na]^+$, ($C_{28}H_{52}N_2NaO_3$ required 487.7138).

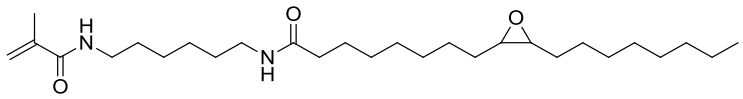
_N_-(6-methacrylamidohexyl)-8-(3-((3-pentyloxiran-2-yl)methyl)oxiran-2-yl)octanamide (SB**(71c))**



The general procedure for the synthesis of fully epoxidised monomers was applied (7.2.3) using SB**(60c)** (20.0 g, 0.04 mol), mCPBA (15.4 g, 0.09 mol) and DCM (200 mL) to produce a white solid (89%). ν_{max}/cm^{-1} 3302 (N-H), 2919, 2849 (C-H), 1634, 1610 (C=O), 1537; δ_H (400MHz, $CDCl_3$): 6.07 (1H, s, NH), 5.80 (1H, s, NH), 5.68 (1H, s, =CH_2), 5.31 (1H, s, =CH_2), 3.30 (2H, apparent dd, *J*=13.0, 6.5, HNCH_2), 3.23 (2H apparent dd, *J*=13.0, 6.5, HNCH_2), 3.19 – 2.80 (4H, m, HC(O)CH), 2.16 (3H, t, *J*=7.5, O=CCH_2), 1.96 (3H, s, CH_3), 1.82 – 1.20 (30H, m, CH_2), 1.06 (0.32H, t,

J=7.5, =CHCH$_2$C<u>H$_3$</u>), 0.95 – 0.83 (3H, m, C<u>H$_3$</u>); δ_C (100MHz, $CDCl_3$): 173.25 (HN<u>C</u>=O), 168.60 (HN<u>C</u>=O), 140.11 (<u>C</u>=CH$_2$), 119.19 (=<u>C</u>H$_2$), 57.26 (H<u>C</u>(O)<u>C</u>H), 57.21 (H<u>C</u>(O)<u>C</u>H), 56.58 (H<u>C</u>(O)<u>C</u>H), 39.17 (HN<u>C</u>H$_2$), 38.95 (HN<u>C</u>H$_2$), 36.80 (O=C<u>C</u>H$_2$), 31.85 (<u>C</u>H$_2$), 29.65 - 29.19 (<u>C</u>H$_2$), 27.84 (<u>C</u>H$_2$), 27.42 (<u>C</u>H$_2$), 26.50 (<u>C</u>H$_2$), 26.03 (<u>C</u>H$_2$), 25.77 (<u>C</u>H$_2$), 22.66 (<u>C</u>H$_2$), 18.72 (<u>C</u>H$_3$), 14.15 (<u>C</u>H$_3$); m/z (ES^+) 515.3 $[M+Na]^+$ HRMS (ES+) 515.3459 $[M+Na]^+$, ($C_{28}H_{48}N_2NaO_5$ required 515.3461); 501.3665 $[M+Na]^+$, ($C_{28}H_{50}N_2NaO_4$ required 501.3668); $[M+Na]^+$; 487.7136 $[M+Na]^+$, ($C_{28}H_{52}N_2NaO_3$ required 487.7138).

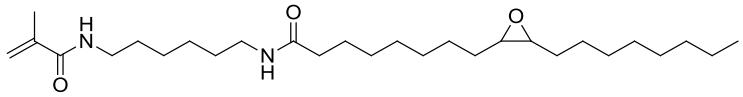
_N_-(6-methacrylamidohexyl)-8-(3-octyloxiran-2-yl)octanamide (PECB**(71c))**



The general procedure for the synthesis of partially epoxidised monomers was applied (7.2.4) using CB**(60c)** (15.0 g, 0.03 mol), mCPBA (0.59 g, 0.003 mol) and DCM (150 mL) to produce a white solid (58%). ν_{max}/cm^{-1} 3307 (N-H), 2918, 2850 (C-H), 1634, 1604 (C=O), 1536, 721 (C=C); δ_H (400 MHz, $CDCl_3$): 5.99 (1H, s, N<u>H</u>), 5.71 – 5.65 (2H, m, N<u>H</u>, =C<u>H$_2$</u>), 5.43 – 5.24 (2H, s, HC=CH, =C<u>H$_2$</u>), 3.31 (2H, apparent dd, *J*=13.0, 7.0, HNCH$_2$), 3.24 (2H, apparent dd, *J*=13.0, 7.0, HNCH$_2$), 2.93 – 2.86 (~1H, m, <u>H</u>C(O)C<u>H</u>), 2.16 (3H, t, *J*=7.5, O=CC<u>H$_2$</u>), 2.10 – 1.98 (3H, m, CH$_2$CH=), 1.97 (3H, s, C<u>H$_3$</u>), 1.71 – 1.42 (12H, m, C<u>H$_2$</u>), 1.42 – 1.18 (28H, m, C<u>H$_2$</u>), 0.87 (3H, t, *J*=6.8, C<u>H$_3$</u>); δ_C (100MHz, $CDCl_3$): 173.41 (HN<u>C</u>=O), 168.56 (HN<u>C</u>=O), 140.21 (<u>C</u>=CH$_2$), 129.99 (H<u>C</u>=<u>C</u>H), 129.76 (H<u>C</u>=<u>C</u>H), 119.23 (C=<u>C</u>H$_2$), 57.24 (<u>C</u>H(O)<u>C</u>H), 39.17 (HN<u>C</u>H$_2$), 38.92 (HN<u>C</u>H$_2$), 36.89 (O=C<u>C</u>H$_2$), 31.93 (CH$_2$), 29.77 - 29.16 (CH$_2$), 27.22 (CH$_2$), 27.18 (CH$_2$), 26.00 (CH$_2$), 25.85 (CH$_2$), 22.68 (CH$_2$),

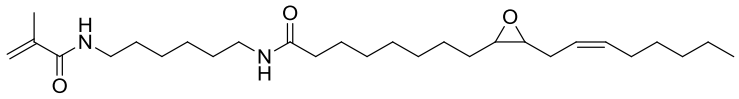
18.73 (<u>C</u>H_3), 14.12 (<u>C</u>H_3); m/z (ES^+) 487.4 $[M+Na]^+$, 473.4 $[M+Na]^+$, 471.4 $[M+Na]^+$, 455.8 $[M+Na]^+$.

***N*-(6-methacrylamidohexyl)-8-(3-octyloxiran-2-yl)octanamide (**PERS**(71c))**



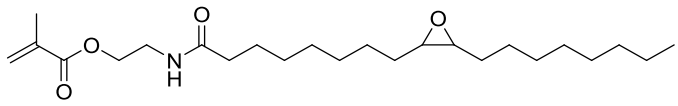
The general procedure for the synthesis of partially epoxidised monomers was applied (7.2.4) using RS**(60c)** (33.0 g, 0.07 mol), mCPBA (9.53 g, 0.06 mol) and DCM (330 mL) to produce a yellow solid (81%). ν_{max}/cm^{-1} 3301 (N-H), 2915, 2849 (C-H), 1634, 1605 (C=O), 1536, 720 (C=C); δ_H (400 MHz, $CDCl_3$); 5.97 (1H, s, N<u>H</u>), 5.68 (1H, s, HN, =CH_2), 5.61 – 5.26 (3H, m, HC=CH, =CH_2), 3.31 (2H, q, *J*=6.5, HNC<u>H</u>$_2$), 3.24 (2H, apparent dd, *J*=13.0, 6.5), 3.18 – 2.71 (2H, m, <u>H</u>C(O)C<u>H</u>), 2.44 – 2.31 (1H, m, =CHC<u>H</u>$_2$CH=), 2.16 (2H, t, *J*=7.5, O=CC<u>H</u>$_2$), 2.10 – 1.98 (2H, m, C<u>H</u>$_2$CH=), 1.96 (3H, s, C<u>H</u>$_3$) 1.68 – 1.18 (34H, m, C<u>H</u>$_2$), 1.09 – 0.95 (0.30H, m, =CHCH$_2$C<u>H</u>$_3$), 0.93 – 0.83 (3H, m, C<u>H</u>$_3$); δ_C (100MHz, $CDCl_3$): 173.31 (HN<u>C</u>=O), 168.56 (O=<u>C</u>NH), 140.25 (<u>C</u>=CH_2), 129.99 (H<u>C</u>=<u>C</u>H), 129.76 (H<u>C</u>=<u>C</u>H), 128.12 (H<u>C</u>=<u>C</u>H), 127.56 (H<u>C</u>=<u>C</u>H) 119.23 (C=<u>C</u>H_2), 57.24 (<u>C</u>H(O)<u>C</u>H), 39.17 (HN<u>C</u>H_2), 38.92 (HN<u>C</u>H_2), 36.89 (O=C<u>C</u>H_2), 31.93 (<u>C</u>H_2), 29.70 - 29.16 (<u>C</u>H_2), 27.22 (<u>C</u>H_2), 26.00 (<u>C</u>H_2), 25.85 (<u>C</u>H_2), 22.62 (<u>C</u>H_2) 22.46 (<u>C</u>H_2), 18.72 (<u>C</u>H_3), 14.15 (<u>C</u>H_3); m/z (ES^+) 501.3 $[M+Na]^+$, 487.4 $[M+Na]^+$, 485.4 $[M+Na]^+$, 471.4 $[M+Na]^+$, 469.3 $[M+Na]^+$.

(Z)-*N*-(6-methacrylamidohexyl)-8-(3-(oct-2-enyl)oxiran-2-yl)octanamide (PESB**(71c))**



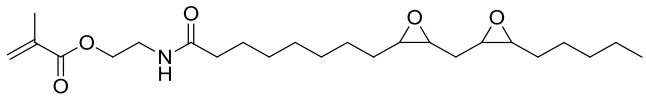
The general procedure for the synthesis of partially epoxidised monomers was applied (7.2.4) using SB**(60c)** (20.0 g, 0.04 mol), mCPBA (7.70 g, 0.04 mol) and DCM (200 mL) to produce a yellow solid, (84%). ν_{max}/cm^{-1} 3302 (N-H), 2917, 2850 (C-H), 1634, 1617 (C=O), 1542, 719 (C=C); δ_H (400 MHz, $CDCl_3$): 5.98 (1H, s, N<u>H</u>), 5.68 (2H, m, NH, =CH_2), 5.61 – 5.26 (3H, m, HC=CH, =CH_2), 3.31 (2H, apparent dd, *J*=6.5, HNCH_2), 3.24 (2H, dd, *J*=13.0, 6.5, HNCH_2), 3.18 – 2.71 (2H, m, <u>H</u>C(O)C<u>H</u>), 2.45 – 2.30 (1H, m, =CHC<u>H_2</u>CH=), 2.16 (2H, t, *J*=7.5, O=CCH_2), 2.06 – 1.98 (3H, m, CH_2CH=), 1.97 (3H, s, C<u>H_3</u>), 1.67 – 1.19 (32H, m, C<u>H_2</u>), 1.09 – 0.94 (0.36H, m, =CHCH_2C<u>H_3</u>), 0.87 (3H, m, C<u>H_3</u>); δ_C (100MHz, $CDCl_3$): 173.38 (HN<u>C</u>=O), 168.23 (O=<u>C</u>NH), 140.19 (<u>C</u>=CH_2), 130.18 (H<u>C</u>=<u>C</u>H), 129.97 (H<u>C</u>=<u>C</u>H), 127.89 (H<u>C</u>=<u>C</u>H), 127.89 (H<u>C</u>=<u>C</u>H), 119.25 (C=<u>C</u>H_2), 57.24 (<u>C</u>H(O)<u>C</u>H), 56.75 (<u>C</u>H(O)<u>C</u>H), 39.17 (HN<u>C</u>H_2), 38.92 (HN<u>C</u>H_2), 36.79 (O=C<u>C</u>H_2), 31.93 (<u>C</u>H_2), 31.52 (<u>C</u>H_2), 29.70 - 29.16 (<u>C</u>H_2), 27.22 (<u>C</u>H_2), 26.00 (<u>C</u>H_2), 25.85 (<u>C</u>H_2), 22.68 (<u>C</u>H_2), 18.73 (<u>C</u>H_3), 14.12 (<u>C</u>H_3); m/z HRMS (ES+) 515.3463 $[M+Na]^+$, ($C_{28}H_{48}N_2NaO_5$ required 515.3461); 501.3665 $[M+Na]^+$, ($C_{28}H_{50}N_2NaO_4$ required 501.3668); $[M+Na]^+$; 487.7136 $[M+Na]^+$, ($C_{28}H_{52}N_2NaO_3$ required 487.7138).

2-(8-(3-octyloxiran-2-yl)octanamido)ethyl methacrylate (RS**(71d))**



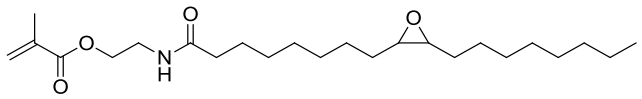
The general procedure for the synthesis of fully epoxidised monomers was applied (7.2.3) using RS**(60d)** (45.0 g, 0.11 mol), mCPBA (29.7 g, 0.17 mol) and DCM (450 mL) to produce a white solid. (42.6 g, 78 %). m.p. 61-65 °C; ν_{max}/cm^{-1} 3304 (N-H), 2917, 2849 (C-H), 1642, 1617 (C=O), 1555, 1238, 716 (C=C); δ_H (400MHz, $CDCl_3$): 6.13 (1H, s, =C$\underline{H}_2$), 6.00 (1H, s, N$\underline{H}$), 5.65 – 5.58 (1H, m, =CH_2), 4.25 (2H, t, *J*=5.5, OC$\underline{H}_2$), 3.57 (2H, q, *J*=5.5, C$\underline{H}_2$NH), 3.23 - 2.84 (3H, m, HC(O)CH), 2.21 (2H, t, *J*=7.5, O=CC$\underline{H}_2$), 1.95 (3H, s, CH_3), 1.69 - 1.19 (26H, m, C$\underline{H}_2$), 1.06 (0.44H, t, *J*=7.5, =CHCH_2C$\underline{H}_3$), 0.88 (3H, t, *J*=6.8, C$\underline{H}_3$); δ_C (100MHz, $CDCl_3$): 173.45 (HNC=O), 167.50 (OC=O), 135.95 (C=CH_2), 126.10 (C=CH_2), 63.47 (OCH_2), 57.26 (HC(O)CH), 57.23 (HC(O)CH), 57.05 (HC(O)CH), 56.99 (HC(O)CH), 38.78 (NHCH_2), 36.62 (O=CCH_2), 31.83 (C$\underline{H}_2$), 29.67 – 29.09 (C$\underline{H}_2$), 27.81 (C$\underline{H}_2$), 27.75 (C$\underline{H}_2$), 26.57 (C$\underline{H}_2$), 25.60 (C$\underline{H}_2$), 22.64 (C$\underline{H}_2$), 18.28 (C$\underline{H}_2$), 14.08 (C$\underline{H}_2$); m/z (ES^+) 460.3 $[M+Na]^+$ HRMS (ES+) 460.2676 $[M+Na]^+$, ($C_{24}H_{39}NNaO_6$ required 460.2675); 446.2887 $[M+Na]^+$, ($C_{24}H_{41}NNaO_5$ required 446.2882); $[M+Na]^+$; 432.3094 $[M+Na]^+$, ($C_{24}H_{43}NNaO_4$ required 432.3090).

2-(8-(3-((3-pentyloxiran-2-yl)methyl)oxiran-2-yl)octanamido)ethyl methacrylate (SB**(71d))**



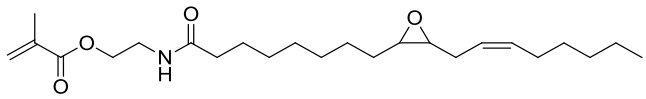
The general procedure for the synthesis of fully epoxidised monomers was applied (7.2.3) using SB**(60d)** (50 g, 0.13 mol), mCPBA (43.9 g, 0.25 mol) and DCM (900 mL) to produce a white solid (83%). ν_{max}/cm^{-1} 3302 (N-H), 2920, 2848 (C-H), 1642, 1617 (C=O), 1555, 1238, 716 (C=C); δ_H (400MHz, $CDCl_3$): 6.13 (1H, s, =C$\underline{H}_2$), 5.92 (1H, s, N$\underline{H}$) 5.60 (1H, s, =C$\underline{H}_2$), 4.25 (2H, t, *J*=5.5, OCH_2), 3.57 (2H, apparent dd, *J*=11.0. 5.5, $\underline{H}_2$CNH), 3.24 – 2.85 (3H, m, $\underline{H}$C(O)C$\underline{H}$), 2.19 (2H, t, *J*=7.5, O=CC$\underline{H}_2$), 1.95 (3H, s, C$\underline{H}_3$), 1.86 – 1.69 (24H, m, C$\underline{H}_2$), 1.06 (0.45H, t, *J*=7.5, =CHCH_2C$\underline{H}_3$), 0.95 – 0.80 (3H, m, C$\underline{H}_3$); δ_C (100MHz, $CDCl_3$): 172.43 (HN$\underline{C}$=O), 166.47 (O$\underline{C}$=O), 134.96 ($\underline{C}$=CH_2), 125.09 (=$\underline{C}H_2$), 62.45 (O$\underline{C}H_2$), 56.26, 56.23, 56.05, 55.76, 53.36, 53.24 (H$\underline{C}$(O)$\underline{C}$H), 37.73 ($H_2\underline{C}$NH), 35.60 (O=C$\underline{C}H_2$), 30.90 (C$\underline{H}_2$), 30.65 (C$\underline{H}_2$), 28.68 – 28.10 (C$\underline{H}_2$), 26.86 (C$\underline{H}_2$), 26.17 (C$\underline{H}_2$), 25.91 (C$\underline{H}_2$), 25.23 (C$\underline{H}_2$), 24.61 (C$\underline{H}_2$), 21.55 (C$\underline{H}_2$), 17.29 (C$\underline{H}_3$), 12.98 (C$\underline{H}_3$); m/z (ES^+) 460.3 $[M+Na]^+$ HRMS (ES+) 460.2677 $[M+Na]^+$, ($C_{24}H_{39}NNaO_6$ required 460.2675); 446.2880 $[M+Na]^+$, ($C_{24}H_{41}NNaO_5$ required 446.2882); $[M+Na]^+$; 432.3087 $[M+Na]^+$, ($C_{24}H_{43}NNaO_4$ required 432.3090).

2-(8-(3-octyloxiran-2-yl)octanamido)ethyl methacrylate (PERS**(71d))**



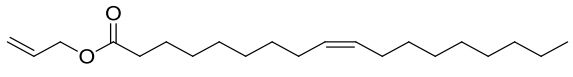
The general procedure for the synthesis of partially epoxidised monomers was applied (7.2.4) using RS**(60d)** (15.0 g, 0.04 mol), mCPBA (4.94 g, 0.03mol) and DCM (150 mL) to produce a yellow solid (80%). ν_{max}/cm^{-1} 3294 (N-H), 2923, 2852 (C-H), 1719, 1646 (C=O), 1542, 720 (C=C); δ_H (300 MHz, $CDCl_3$): 6.20 (1H, s, NH), 6.07 – 5.99 (1H, m, =CH_2), 5.54 – 5.46 (1H, m, =CH_2), 5.43 – 5.11 (2H, m, HC=CH), 4.14 (2H, t, *J*=5.5, OCH_2), 3.46 (2H, apparent dd, *J*=11.0, 5.5,HNCH_2), 3.07 – 2.58 (2H, m, HC(O)CH), 2.09 (2H, t, *J*=7.5, O=CCH_2), 2.03 – 1.87 (3H, m, CH_2CH=), 1.87 – 1.79 (3H, m, CH_3), 1.62 – 1.05 (30H, m, CH_2), 1.01 – 0.84 (0.70H, m, =CHCH_2CH_3), 0.84 – 0.72 (3H, m, CH_3); δ_C (100MHz, $CDCl_3$): 173.47 (HNC=O), 167.42 (OC=O), 135.94 (C=CH_2), 129.95 (HC=CH), 129.67 (HC=CH), 128.01 (HC=CH), 127.86 (HC=CH), 126.02 (=CH_2), 63.41 (OCH_2), 57.32 (HC(O)CH), 56.67 (HC(O)CH), 38.69 (HNCH_2), 36.63 (O=CCH_2), 31.87 (CH_2), 29.72 - 29.11 (CH_2), 27.17 (CH_2), 25.68 (CH_2), 25.59 (CH_2), 22.64 (CH_2), 18.25 (CH_3), 14.07 (CH_3); m/z HRMS (ES+) 446.2885 $[M+Na]^+$, ($C_{24}H_{41}NNaO_5$ required 446.2882); 444.2723 $[M+Na]^+$, ($C_{24}H_{39}NNaO_5$ required 44.2726); 432.3088 $[M+Na]^+$, ($C_{24}H_{43}NNaO_4$ required 432.3090) 430.2930 $[M+Na]^+$, ($C_{24}H_{41}NNaO_4$ required 430.2933); 416.3139 $[M+Na]^+$, ($C_{24}H_{43}NNaO_3$ required 416.3141).

(Z)-2-(8-(3-(oct-2-enyl)oxiran-2-yl)octanamido)ethyl methacrylate (PESB**(71d))**



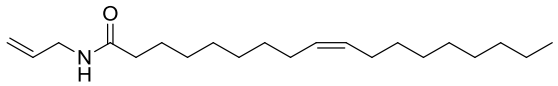
The general procedure for the synthesis of partially epoxidised monomers was applied (7.2.4) using SB**(60d)** (21.5 g, 0.05 mol), mCPBA (9.44 g, 0.05 mol) and DCM (215 mL) to produce a yellow solid (87%). ν_{max}/cm^{-1} 3297 (N-H), 2925, 2846 (C-H), 1719, 1648 (C=O), 1542, 721 (C=C); δ_H (400MHz, $CDCl_3$): 6.13 (1H, s, =C$\underline{H}_2$), 5.88 (1H s, N$\underline{H}$), 5.60 (1H, s, =C$\underline{H}_2$), 5.57 – 5.27 (2H, m, $\underline{H}$C=C$\underline{H}$), 4.25 (2H, t, *J*=5.5, OC$\underline{H}_2$), 3.57 (2H, q, *J*=5.5, HNC$\underline{H}_2$), 3.25 – 2.70 (2H m, $\underline{H}$C(O)C$\underline{H}$), 2.18 (2H t, *J*=7.5, O=CH_2), 2.11 – 1.99 (1H, m, CH_2CH=), 1.95 (3H, m, C$\underline{H}_3$), 1.78 – 1.17 (28H, m, C$\underline{H}_2$), 1.09 – 0.95 (0.36H, m, =CHCH_2C$\underline{H}_3$), 0.95 – 0.84 (3H m, C$\underline{H}_3$); δ_C (100 MHz, $CDCl_3$): 173.37 (HN$\underline{C}$=O), 167.47 (O$\underline{C}$=O), 135.96 ($\underline{C}$=CH_2), 130.20 (H$\underline{C}$=$\underline{C}$H), 130.00 (H$\underline{C}$=$\underline{C}$H), 128.03 (H$\underline{C}$=$\underline{C}$H), 127.88 (H$\underline{C}$=$\underline{C}$H), 126.07 (H$\underline{C}$=$\underline{C}$H), 63.48 (O$\underline{C}H_2$), 57.64 (H$\underline{C}$(O)$\underline{C}$H), 57.12 (H$\underline{C}$(O)$\underline{C}$H), 56.67 (H$\underline{C}$(O)$\underline{C}$H), 56.72 (H$\underline{C}$(O)$\underline{C}$H), 38.75 (HN$\underline{C}H_2$), 36.68 (O=C$\underline{C}H_2$), 31.90 ($\underline{C}H_2$), 31.50 ($\underline{C}H_2$), 29.75 - 29.23 ($\underline{C}H_2$), 27.18 ($\underline{C}H_2$), 25.68 ($\underline{C}H_2$), 25.61 ($\underline{C}H_2$), 22.66 ($\underline{C}H_2$), 22.55 ($\underline{C}H_2$), 18.29 ($\underline{C}H_3$), 14.07 ($\underline{C}H_3$); m/z HRMS (ES+) 446.2886 $[M+Na]^+$, ($C_{24}H_{41}NNaO_5$ required 446.2882); 444.2724 $[M+Na]^+$, ($C_{24}H_{39}NNaO_5$ required 44.2726); 432.3092 $[M+Na]^+$, ($C_{24}H_{43}NNaO_4$ required 432.3090) 430.2931 $[M+Na]^+$, ($C_{24}H_{41}NNaO_4$ required 430.2933); 416.3138 $[M+Na]^+$, ($C_{24}H_{43}NNaO_3$ required 416.3141) 414.2986 $[M+Na]^+$, ($C_{24}H_{41}NNaO_3$ required 414.2984).

allyl oleate (RS**(77a))**



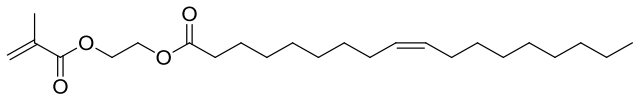
Rapeseed oil (10 g, 0.01 mol, 1 equiv.) and allyl alcohol (1.94 g, 2.27 mL, 0.03 mol, 3 equiv.) heated to 60 °C under a nitrogen atmosphere. The reaction mixture was dissolved in diethyl ether (50 mL), washed with water (2 X 50 mL) and dried over Na_2SO_4, filtered and dried in *vacuo* to produce crude product. Crude product purified using column chromatography eluting with 12:1 hexane/diethyl ether, to give RS**(77a)** (72%) as a clear oil. R_f = 0.5 (12:1 hexane:diethyl ether); ν_{max}/cm^{-1} 3080 (C=CH_2), 2920, 2851 (C-H), 1741 (C=O), 1543, 986 , 721 (C=C); δ_H (400MHz, $CDCl_3$): 6.00 – 5.84 (1H, m, H_2=CC<u>H</u>CH_2O), 5.40 – 5.31 (3H, m, <u>H</u>C=C<u>H</u>), 5.29 – 5.21 (2H, m, <u>H_2</u>C=CHC), 4.57 (2H, dt, *J*=5.7, 1.4, H_2=CCHC<u>H_2</u>O), 2.84 – 2.73 (1H, m, HC=CHC<u>H_2</u>CH=CH), 2.33 (2H, t, *J*=7.6, O=CC<u>H_2</u>), 2.10 – 1.95 (4H, m <u>H_2</u>CCH=CH), 1.69 – 1.58 (2H, m, O=CCH_2C<u>H_2</u>), 1.28 (24H, m, C<u>H_2</u>), 0.97 (1H, t, *J*=7.5, =CH_2CH_2C<u>H_3</u>), 0.92 – 0.84 (3H, m, C<u>H_3</u>); δ_C (100MHz, $CDCl_3$): 173.48 (O<u>C</u>=O), 132.36 (H_2=C<u>C</u>HCH_2O), 130.20 - 127.91 (H<u>C</u>=<u>C</u>H), 118.04 (H_2<u>C</u>=CHC), 64.91 (H_2=CCH<u>C</u>H_2O), 34.26 (O=C<u>C</u>H_2), 31.91 (<u>C</u>H_2), 29.77 - 29.09 (<u>C</u>H_2), 27.22 (<u>C</u>H_2), 27.16 (<u>C</u>H_2), 25.63 (<u>C</u>H_2), 24.95 (<u>C</u>H_2), 22.68 (<u>C</u>H_2), 14.11 (<u>C</u>H_3); m/z (ES^+) 345.3 $[M+Na]^+$ HRMS (ES+) 345.2764 $[M+Na]^+$, ($C_{21}H_{38}NaO_2$ required 345.2770); 343.2608 $[M+Na]^+$, ($C_{21}H_{36}NaO_2$ required 343.2613); 341.2451 $[M+Na]^+$, ($C_{21}H_{38}NaO_2$ required 341.2457).

***N*-allyloleamide (**RS**(77b))**



Rapeseed oil (10 g, 0.01 mol, 1 equiv.) and allylamine (1.97g, 2.59 mL, 0.03 mol, 3 equiv.) reacted at room temperature for 24 h under a nitrogen atmosphere. The reaction mixture was dissolved in diethylether (50 mL), washed with water (2 X 50 mL) and dried over Na_2SO_4, filtered and dried in *vacuo* to produce crude product. Crude product purified using column chromatography eluting with 2:1 pet ether/EtOAc, to give RS**(77b)** (56%) as a white solid. R_f = 0.45 (2:1 pet ether:EtOAc); ν_{max}/cm^{-1} 3297 (N-H), 3079 (vinyl), 2922, 2852 (C-H), 1697 (C=O), 1262, 1033 (C-O), 989, 721 (C=C); δ_H (400MHz, $CDCl_3$): 5.84 (1H, ddt, *J*=15.9, 10.3, 5.7, H_2=CC<u>H</u>CH_2NH), 5.44 (1H, s, N<u>H</u>), 5.41 – 5.29 (3H, m, <u>H</u>C=C<u>H</u>), 5.21 – 5.11 (2H, m, <u>H_2</u>C=CHC), 3.89 (2H, tt, *J*=5.7, 1.5, H_2=CCHC<u>H_2</u>NH), 2.87 – 2.72 (1H, m, HC=CHC<u>H_2</u>CH=CH), 2.19 (2H, t, *J*=7.6, O=CC<u>H_2</u>), 2.10 – 1.96 (4H, m, <u>H_2</u>CCH=CH), 1.69 – 1.59 (2H, m, O=CCH_2C<u>H_2</u>), 1.38 – 1.21 (24H, m, C<u>H_2</u>), 0.98 (~1H, t, *J*=7.5, =CH_2CH_2C<u>H_3</u>), 0.91 – 0.85 (3H, m, C<u>H_3</u>); δ_C (100MHz, $CDCl_3$): 172.98 (HN<u>C</u>=O), 134.38 (H_2=C<u>C</u>HCH_2NH), 130.02 (H<u>C</u>=<u>C</u>H), 129.76 (H<u>C</u>=<u>C</u>H), 116.35 (H_2<u>C</u>=CHC), 41.89 (H_2=CCH<u>C</u>H_2NH), 36.83 (O=C<u>C</u>H_2), 29.77 – 29.14 (<u>C</u>H_2), 27.23 (<u>C</u>H_2), 27.18 (<u>C</u>H_2), 25.78 (<u>C</u>H_2), 22.69 (<u>C</u>H_2), 14.13 (<u>C</u>H_3); m/z (ES^+) 344.3 $[M+Na]^+$ HRMS (ES+) 344.2934 $[M+Na]^+$, ($C_{21}H_{39}NNaO$ required 344.2929); 342.2767 $[M+Na]^+$, ($C_{21}H_{37}NNaO$ required 342.2773); $[M+Na]^+$; 340.2611 $[M+Na]^+$, ($C_{21}H_{35}NNaO$ required 340.2616).

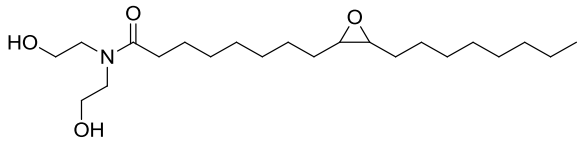
2-(methacryloyloxy)ethyl oleate (80)



Rapeseed oil (10 g, 0.01 mol, 1 equiv.), HEMA (4.42 g, 4.15 mL, 0.03 mol, 3 equiv.) and NaOMe (0.5 g) reacted at room temperature under N_2 for 24 h. Reaction mixture dissolved in DCM (50 mL) and washed with water (2 X 50 mL), dried over Na_2SO_4 and solvent removed in *vacuo* to give a crude yellow oil. Crude product purified using column chromatography eluting with 9:1 pet ether/EtOAc, to give (**80)** (70%) as a clear oil. R_f = 0.5 (9:1 pet ether:EtOAc); ν_{max}/cm^{-1} 2920, 2851 (C-H), 1741 (C=O), 1543 (), 986 (), 721 (C=C); δ_H (400MHz, CDCl3): 6.13 (1H, s, =C$\underline{H}_2$), 5.61 - 5.58 (1H, m, =C$\underline{H}_2$), 5.44 – 5.27 (3H, m, $\underline{H}$C=C$\underline{H}$), 4.37 – 4.29 (4H, m, OC$\underline{H}_2$C$\underline{H}_2$O), 2.85 – 2.71 (1H, m, HC=CHC$\underline{H}_2$CH=CH), 2.32 (2H, t, *J*=7.5, O=CC$\underline{H}_2$), 2.12 – 1.97 (4H, m, $\underline{H}_2$CCH=CH), 1.95 (3H, s, C$\underline{H}_3$), 1.68 – 1.56 (2H, m, O=CCH$_2$C$\underline{H}_2$), 1.40 – 1.20 (22 H, m, C$\underline{H}_2$), 0.97 (1H, t, *J*=7.5, =CH$_2$CH$_2$C$\underline{H}_3$), 0.88 (3H, t, *J*=6.9, C$\underline{H}_3$); δ_C (100MHz, $CDCl_3$): 173.50 (O$\underline{C}$=O), 167.03 (O$\underline{C}$=O), 135.95 (H$_3$C$\underline{C}$=C), 130.17 - 127.73 (H$\underline{C}$=$\underline{C}$H), 125.92 (H$_2\underline{C}$=CH), 62.44 (O$\underline{C}$H$_2$), 61.84 (O$\underline{C}$H$_2$), 34.11 (O=C$\underline{C}$H$_2$), 31.89 ($\underline{C}$H$_2$), 29.75 - 29.07 ($\underline{C}$H$_2$), 27.14 ($\underline{C}$H$_2$), 24.89 ($\underline{C}$H$_2$), 22.66 ($\underline{C}$H$_2$), 18.23 ($\underline{C}$H$_3$), 14.08 ($\underline{C}$H$_3$); m/z (ESI) 417.2975 $[M+Na]^+$, HRMS (ES+) ($C_{24}H_{42}NaO_4$ required 417.2981); 415.2819 $[M+Na]^+$, ($C_{24}H_{40}NaO_4$ required 415.2824); 413.2662 $[M+Na]^+$, ($C_{24}H_{38}NaO_4$ required 413.2668).

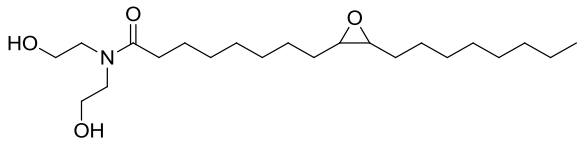
7.3 Synthesis of Diols for use in Chapter 4

N,N-bis(2-hydroxyethyl)-8-(3-octyloxiran-2-yl)octanamide (CB(102))



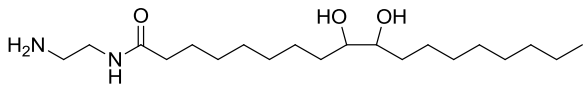
Epoxidised cocoa butter (20 g, 0.02mol, 1 equiv.), diethanolamine (10.8 g, 0.10 mol, 4.5 equiv.) and sodium methoxide (3.18 g) heated to 100 °C for 6 hours. Reaction mixture dissolved in DCM (200 mL) and washed with water (252 mL), dried over Na_2SO_4 and solvent removed in *vacuo* to give a light yellow waxy solid, (87%). ν_{max}/cm^{-1} 3391 (OH), 2923, 2854 (C-H), 1618 (C=O); δ_H (400 MHz, $CDCl_3$): 4.12 (2H, s, O<u>H</u>), 3.80 (2H, t, *J*=5.0, HOC<u>H</u>$_2$), 3.76 (2H, t, *J*=5.0, HOC<u>H</u>$_2$), 3.53 (1H, t, *J*=5.0, <u>H</u>$_2$CN), 3.49 (1H, t, *J*=5.0, <u>H</u>$_2$CN), 2.95 – 2.86 (1H, m, C<u>H</u>(O)C<u>H</u>), 2.43 – 2.32 (2H, m, O=CC<u>H</u>$_2$), 1.71 – 1.56 (2H, m, C<u>H</u>$_2$CH(O)CHC<u>H</u>$_2$), 1.56 – 1.43 (2H, m, O=CCH$_2$C<u>H</u>$_2$), 1.39 – 1.20 (22H, m, <u>C</u>H$_2$), 0.88 (3H, t, *J*=6.5, C<u>H</u>$_3$); δ_C (101 MHz, $CDCl_3$): 175.66 (O<u>C</u>=O), 61.28, 60.73 (HO<u>C</u>H$_2$), 57.33 (<u>C</u>H(O)<u>C</u>H), 52.25 (H$_2$<u>C</u>N), 50.56 (H$_2$<u>C</u>N), 33.63 (O=C<u>C</u>H$_2$), 31.91 (<u>C</u>H$_2$), 29.69 - 29.21 (<u>C</u>H$_2$), 27.81 (<u>C</u>H$_2$), 27.76 (<u>C</u>H$_2$), 26.59 (<u>C</u>H$_2$), 25.32 (<u>C</u>H$_2$), 22.67 (<u>C</u>H$_2$), 14.11 (<u>C</u>H$_3$); m/z (ES^+) 408.3 [$M+Na^+$]; 394.3 [$M+Na^+$]; 366.2 [$M+Na^+$]; HRMS (ES+) 408.3092 [$M+Na^+$] ($C_{22}H_{43}NNaO_4$ required 408.3090); 394.3299 [$M+Na^+$] ($C_{22}H_{45}NNaO_3$ required 394.3297) 366.2986 [$M+Na^+$] ($C_{20}H_{41}NNaO_3$ required 366.2984).

***N,N*-bis(2-hydroxyethyl)-8-(3-octyloxiran-2-yl)octanamide (**RS**(102))**



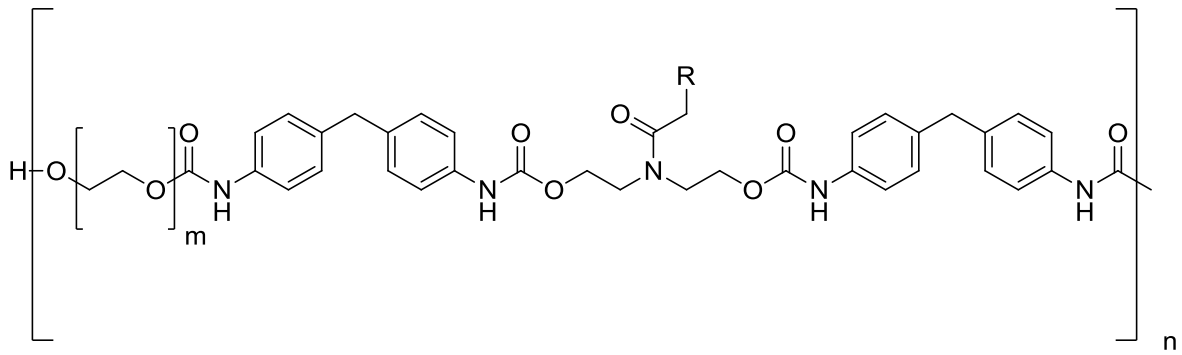
Epoxidised rapeseed oil (20 g, 0.02 mol, 1 equiv.), diethanolamine (10.4 g, 0.09 mol, 4.5 equiv.) and sodium methoxide (3.18 g) heated to 100 °C for 6 hours. Reaction mixture dissolved in DCM (200 mL) and washed with water (250 mL), dried over Na_2SO_4 and solvent removed in *vacuo* to give a dark orange viscous oil, (89%). ν_{max}/cm^{-1} 3395 (OH), 2916, 2849 (C-H), 1618 (C=O) 720 (C=C); δ_H (400 MHz, $CDCl_3$): 4.14 (2H, s, O<u>H</u>), 3.81 (2H, t, *J*=5.0, HOC<u>H</u>$_2$), 3.76 (2H, t, *J*=5.0, HOC<u>H</u>$_2$), 3.53 (1H, t, *J*=5.0, <u>H</u>$_2$CN), 3.49 (1H, t, *J*=5.2, <u>H</u>$_2$CN), 2.95 – 2.86 (3H, m, C<u>H</u>(O)C<u>H</u>), 2.85 – 2.71 (1H, m, =CHC<u>H</u>$_2$CH=), 2.38 (2H, t, *J*=7.5, O=CC<u>H</u>$_2$), 1.71 – 1.53 (2H, m, O=CCH$_2$C<u>H</u>$_2$), 1.56 – 1.43 (3H, m, C<u>H</u>$_2$CH(O)CHC<u>H</u>$_2$), 1.40 – 1.20 (22H, m, <u>C</u>H$_2$), 0.98 (0.14, t, *J*=7.5, =CHCH$_2$C<u>H</u>$_3$), 0.88 (3 H, t, *J*=6.5, C<u>H</u>$_3$); δ_C (101 MHz, $CDCl_3$) 175.67 (N=O), 61.33 (HO<u>C</u>H$_2$), 60.76 (HO<u>C</u>H$_2$), 57.33 (<u>C</u>H(O)<u>C</u>H), 56.74 (<u>C</u>H(O)<u>C</u>H), 52.27 (H$_2$<u>C</u>N), 50.58 (H$_2$<u>C</u>N), 33.63 (O=C<u>C</u>H$_2$), 31.51 (<u>C</u>H$_2$), 29.75 - 29.21 (<u>C</u>H$_2$), 27.20 (<u>C</u>H$_2$), 25.62 (<u>C</u>H$_2$), 25.30 (<u>C</u>H$_2$), 22.68 (<u>C</u>H$_2$), 22.57 (<u>C</u>H$_2$), 14.08 (<u>C</u>H$_3$); m/z (ES^+) 422.3 [M+Na^+]; 408.3 [M+Na^+]; HRMS (ES+) 422.2883 [M+Na^+] ($C_{22}H_{41}NNaO_5$ required 422.2882); 408.3091 [M+Na^+] ($C_{22}H_{43}NNaO_4$ required 408.3090).

***N*-(2-aminoethyl)-9,10-dihydroxyoctadecanamide (**RS**(104a))**



Ring-opened rapeseed oil (20 g, 0.02 mol, 1 equiv.), ethylenediamine (5.4 g, 0.09 mol, 4.5 equiv.) and sodium methoxide (3.24 g) heated to 60 °C under a nitrogen atmosphere for 6 hours. Reaction mixture dissolved in DCM (50 mL) and washed with NaCl, dried over Na_2SO_4 and solvent removed in *vacuo* to give a yellow waxy solid, (80%). ν_{max}/cm^{-1} 3289 (N-H, OH), 2916, 2848 (C-H), 1636, 1633 (C=O), 1549 (N-H); δ_H (300 MHz, $CDCl_3$): 6.23 (1H, s, N<u>H</u>), 3.27 (2H, dd, *J*=11.0, 5.5, HNC<u>H</u>$_2$), 2.90 – 2.75 (2H m, H_2NC<u>H</u>$_2$), 2.15 (2H, t, *J*=7.0, O=CC<u>H</u>$_2$), 1.73 – 1.10 (24H, m, C<u>H</u>$_2$), 0.88 (3H, t, *J*=6.5, C<u>H</u>$_3$); m/z (ES^+) 391.3 [$M+H^+$]; 359.3 [$M+H^+$]; HRMS (ES+) 413.2993 [$M+Na^+$] ($C_{20}H_{42}N_2NaO_5$ required 413.2991); 381.3096 [$M+Na^+$] ($C_{20}H_{42}N_2NaO_5$ required 381.3093).

7.4 Polyurethane Preparations for Chapter 4



Polyol (1 equiv.) and biopolymer (1 equiv.) dissolved in chloroform and flushed with nitrogen for 30 minutes. MDI (2 equiv.) added and refluxed at 65 °C under a nitrogen atmosphere for 24 h. Reaction mixture cooled and ~ 90 % of the chloroform

removed in *vacuo*. Mixture poured into a mould pre-greased with a thin layer of vacuum grease, and cured in oven at 50 °C for 24 h, followed by 24 h in vacuum oven to insure removal of all solvent and proper curing of polymer.

7.5 Oligomerisation with $BF_3.Et_2O$ for Chapter 5

Epoxidised diol (5 g, 0.01 mol, 1 eq.) in DCM (30 mL) under nitrogen until dissolved. $BF_3.Et_2O$ (0.97 g, 0.84 mL, 0.005 mol, 0.5 eq.) added and heated at 40 °C for 24 h. Reaction mixture washed with water and dried over Na_2SO_4 and concentrated in *vacuo* to give product, no further purification was undertaken.

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Appendices

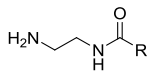
Appendix A

Compound numbering key

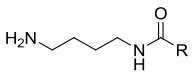
Compounds were made with three different triglycerides cocoa butter (CB), rapeseed oil (RS) or soybean oil (SB). Either CB, RS, or SB were shown before the compound number (in brackets) to denote which triglyceride was used at any particular time (e.g. CB**(61a)** denotes a compound derived from cocoa butter).

R denotes a fatty acid chain either saturated (palmitic or stearic) or unsaturated (oleic, linoleic or linolenic), this is dependent on the starting triglyceride (see Table 2.1, for fatty acid compositions for triglycerides used).

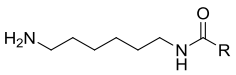
Amides



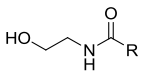
(61a)



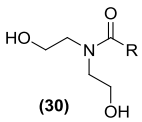
(61b)



(61c)

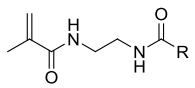


(61d)

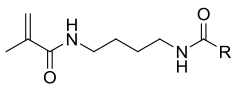


(30)

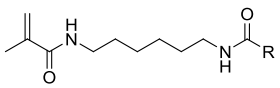
Unsaturated monomers



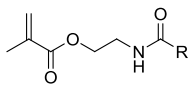
(60a)



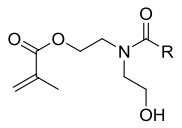
(60b)



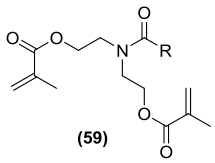
(60c)



(60d)



(58)



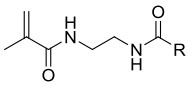
(59)

Epoxidised monomers

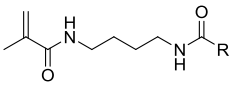
Partially epoxidised monomers are prefixed with PE (e.g. PECB**(71a)**).

R denotes fatty acid chain. With the epoxidised monomers the fatty acid chain can either be unsaturated or epoxidised, dependent on the degree of epoxidation. When partially epoxidised (PE), approximately 50% (from NMR) of double bonds have

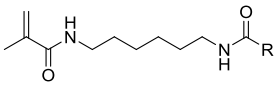
been epoxidised. When fully epoxidised 100 % of double bonds have been epoxidised.



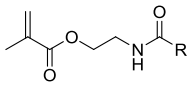
(71a)



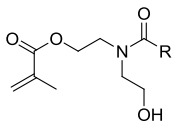
(71b)



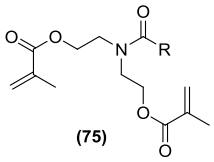
(71c)



(71d)

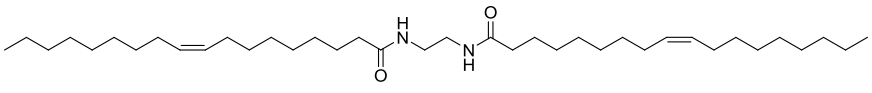


(74)

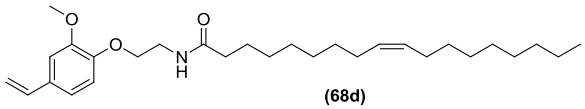


(75)

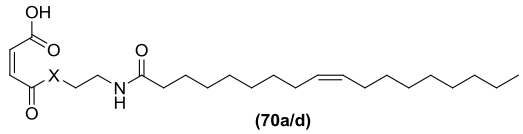
Other monomers



(63a)

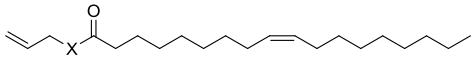


(68d)



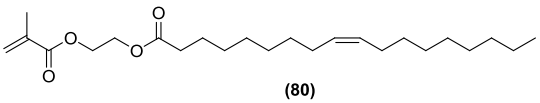
(70a) X = NH
(70d) X = O

(70a/d)



(77a) X = O
(77b) X = NH

(77a-b)



(80)

Appendix B

GPC results for latexes in Chapter 3.

Linker	Triglyceride	Mn (KDa)	Mw (KDa)	PDI
58/59	Cocoa Butter	19.0	3669.0	-
	Rapeseed Oil	4.7	13.0	2.74
	Soybean Oil	2.9	147.5	
60d	Rapeseed oil	28.3	145.0	-
	Soybean oil	463.8	2.3E+4	-
60a	Cocoa Butter	70.2	198.5	2.83
	Rapeseed Oil	19.6	57.0	2.92
	Soybean Oil	10.2	1.8E+4	-
60b	Cocoa Butter	9.8	5.3E+4	-
	Rapeseed Oil	16.3	42.6	2.62
	Soybean Oil	15.0	1.7E+4	-
60c	Cocoa Butter	10.6	1.9E+4	-
	Rapeseed Oil	5.3	1639.0	-
	Soybean Oil	9.8	1.8E+4	-

Unsaturated polymer latexes GPC results (- denotes PDI of >10)

Linker	Triglyceride	Mn (KDa)	Mw (KDa)	PDI
74/75	Rapeseed Oil	10.3	5151.0	-
	Soybean Oil	8.2	1.7E+4	-
71a	Rapeseed Oil	37.3	88.6	2.37
	Soybean Oil	7.2	8587.0	-
71b	Rapeseed Oil	26.2	1.9E+5	-
	Soybean Oil	16.4	1.8E+4	-
71c	Rapeseed Oil	25.2	81.3	3.22
	Soybean Oil	16.4	1.6E+4	-

Partially epoxidised polymer latexes GPC results (- denotes PDI of >10)

Linker	Triglyceride	Mn (KDa)	Mw (KDa)	PDI
71b	Rapeseed Oil	279.5	1000.0	3.6
71c	Rapeseed Oil	22.8	63.3	2.77

Fully epoxidised polymer latexes GPC results (- denotes PDI of >10)

Appendix C

Cross-linking density

The solvent swelling measurements (Chapter 4) were used to find the swelling ratio (q). This can be defined as the inverse of the equilibrium volume fraction of the polymer (V_p). It was calculated using the following equations.

$$Q = \frac{(W_1 - W_0)p_p}{W_0 p_p}$$

(Equation 1)

and

$$q = 1 + Q = \frac{1}{V_p}$$

(Equation 2)

where W_0 and W_1 are the sample weights before and after swelling, respectively, p_s is the density of the solvent (toluene = 0.87) and p_p is the density of the polymer sample.

The average molecular weight between cross-links (M_c) and subsequently the cross-link density (v_c) can then be calculated using the Flory-Rehner equation.

$$M_c = \frac{\bar{\upsilon}_s p_p (V_p^{\frac{1}{3}} - \frac{V_p}{2})}{\ln(1 - V_p) + V_p + \chi V_p^2}$$

(Equation 3)

and

$$v_c = \frac{p_p}{M_c}$$

(Equation 4)

Here $\bar{\upsilon}_s$ is the molar volume of the solvent, χ is the interaction parameter for the solvent-network system, which is calculated using the solubility parameters from the following equation:

$$\chi = \beta + \frac{\bar{\upsilon}_s(\delta_p - \delta_s)^2}{RT}$$

(Equation 5)

where β is the lattice constant (0.34), δ_p is the solubility parameter for the polymer (8.9) and δ_s is the solubility parameter for the solvent (toluene = 10.0).